VOL. VI. No. 62. JULY, 1942

Plastics

Dealing with the Manufacture, Uses and Potentialities of Plastic Materials

Proprietors - TEMPLE PRESS LIMITED
Managing Director ROLAND E. DANGERFIELD

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Post-war Houses

WHILE we are all quite clear that the war must be finished and won first, we are told that we must prepare the solution of post-war problems. These in many ways sometimes seem vaster than the conduct of the war itself. Feeding of the nations that have been deliberately starved in Europe and elsewhere by the enemy will be perhaps the first consideration. The housing of them and of those who have had their homes smashed in this and other countries comes high on the list of succeeding problems. And when we consider that normal repair of non-destroyed houses and factories has virtually stopped, that a better life after the war means complete clearance of slums, better houses, better and more hospitals, improved schools and playgrounds, etc., etc., the problem, which, socially speaking, has a time limit for completion to prevent world dissatisfaction, is indeed almost overwhelming. Great Britain will have to provide not only for her own growing deficiencies but will have to export at the same time.

How is all this to be prepared for in detail in war-time and set into operation as soon as peace is declared?

One thing that stands out as of prime importance is that a new method of building houses must be evolved.

In the month of June we attended a Press meeting invoked by a recently formed body known as the Committee for the Industrial and Scientific Provision of Housing which has its offices in Albemarle Street, London, W.1. The problem which faces us was concisely put by the Chairman, Mr. Harry Weston, M.I.Prod.E., who is also chairman of the City of Coventry Housing Committee and managing director of Modern Machine Tools, Ltd.

He told us that, so far, 3,000,000 houses are required in this country alone and that at the pre-war rate of building this would take some 10 years to accomplish. This is quite apart, of course, from the number of factories, offices and other structures that will be needed. These figures give us a faint idea of the magnitude of the task. The only solution appears to be the application of mechanization on a big scale to the production of building components, and while Government and other research bodies investigate the type of materials best suitable to building, there does not exist any unit which deals with the manufacturing methods of producing homes. Furthermore, Mr. Weston said, it appears strange that while in the last 30 years the price of the motorcar has diminished from, say, £300 to £150, with improved performance, the price of houses has increased enormously. There is doubt whether they have improved with increased cost.

The new Committee therefore is investigating as prime studies the following two problems.

Can the industrial assembly-line method be applied to the solution of post-war housing?

Is it possible by mass-production to produce houses socially, æsthetically, and economically desirable?

Obviously, with the possible exception of brick-making, the present building industry is not built up on mass-producing lines. Far less so are the methods of erection of houses, and yet each of the raw materials is capable of being so treated. The Committee therefore proposes to investigate the possibilities of each and all of them, and it is interesting to note that in its opinion plastics must be considered as important raw materials for the production of structures and examined as individuals or co-ordinated with the older building materials. Plastics, like metals, wood and concrete, lend themselves admirably to the system of prefabrication. The possibilities in house production have already been indicated in these pages by several writers.

The Committee for the Industrial and Scientific Provision of Housing is not formed for the purpose of profit. It consists of a number of technicians, professional and industrial, who have joined together on a voluntary basis. It is financed by donations and payments by industrial concerns, organizations and institutions.

Sweet Music and Sour

IN the quieter days we might have put the following note in what we used to call, perhaps somewhat euphemistically, our Ideas Page. Although this section has been allowed to lapse owing to stultification of the Editorial war-time brain, it is hoped to reinstate it from time to time.

Anybody who has handled a piece of Nylon, especially of the thicker surgical "catgut" (0.02-in. diam.) no doubt immediately thinks of its suitability for violin strings. We were fortunate in being able to secure a long piece from I.C.I., Ltd., under the pretence that we were doing some secret research work for the Government. We handed it to a well-known violinist "warden-post" friend and told him to try it out as an E string, merely saying it was a synthetic material.

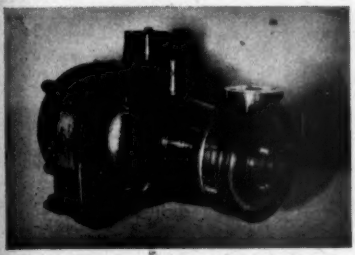
He returned in a day or so, full of enthusiasm, saying that it was an outstanding success and gave a tone purer even than natural "catgut." He immediately devised a sales system for us whereby we were to make our fortunes. We gently explained the situation—that we neither made nylon in the Bowling Green Lane offices, that none could be obtained in war-time for any but important uses, nor was the idea very original. While our stock dropped somewhat we have nevertheless gained an enviable reputation as a chemical wizard.

A few days later our stock dropped still more, for the famous violinist gave us the dreadful news that a period of beautiful music is always followed by a sudden squeaking noise, and he wanted to know why. Now, our knowledge and appreciation of music is about equal to our knowledge and appreciation of the love-life of pterodactyls. We dislike Bach's music merely because Professor Joad loves it and we have forgotten the little we know about sound, so we cannot give much of an answer. The smoothness of the nylon string is perhaps responsible, reducing greatly the friction of the rosin. The normal twisted natural string with its inequalities obviously helps in maintaining the friction. An interesting possibility might be the production of an indented nylon thread, which if successful would help considerably a section of the community that makes life more pleasant for us.[9] If any reader can give a real reason why the string squeaks we shall be glad to pass on the information.

(Note: On second thoughts we are somewhat doubtful about putting the blame on the smoothness of the string. No similar trouble is encountered when using steel strings, which are even smoother than nylon.)

Cast Resins in Engineering

THE interest that has been shown in the use of transparent cast resins grows apace. Readers will remember the excellent examples made by J. Burns and Co., Ltd., and by Runcolite, Ltd., in the form of gears, pumps, connecting rods, etc., made for purely scientific or experimental purposes, which we reproduced in this journal some months ago.



Experimental motor-driven Mopump machined from Catalin cast resin.

The latest example comes from Stockport—from the well-known engineering works of Rhodes, Brydon and Youatt, Ltd. Mr. Youatt has forwarded us a photograph of a pump which they have machined from a solid block of Catalin (cast phenolic resin). This pump is, in effect, the same as the company's Mopump No. 846, which normally has a body and cover of cast iron. Mr. Youatt tells us that the new resin pump is purely experimental and that the present bronze impeller will, in due course, be replaced for experimental purposes by a cast resin one. We shall await results with considerable interest.

Shellac Moulding Powder

WE have previously mentioned in these pages the important researches that have been carried out in India by the London Shellac Research Bureau on the moulding of shellac. The most recent work is that related in the Journal of the Institute of Chemists (India) under the title of "Shellac in Injection Moulding," by Y. Sankaranarayananan, M.Sc., and H. K. Sen, D.Sc. The authors describe a mixture of 30 parts by weight of shellac (30 mesh), 20 parts jute (12-18 mesh) and 32 parts of a mixture of kaolin, pigment and lubricant, which, on treatment with ammonia, is ready for use as an injection moulding powder.

Whilst no claim is made that the mouldings formed from this mixture are comparable with acetate or polystyrene mouldings (shellac does not produce transparent or colourless products) they are, nevertheless, cheap and strong.

SAVE PAPER

More than ever is paper waste required for our war industries. More than ever is it urgent that all factories and offices should ransack their cupboards and old files for unwanted, superfluous and out-of-date records. Waste paper makes munitions in a hundred forms—from shell cases to aeroplane parts.

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PLASTICS: *Their Origin and Formation*

4.—POLYVINYL RESINS

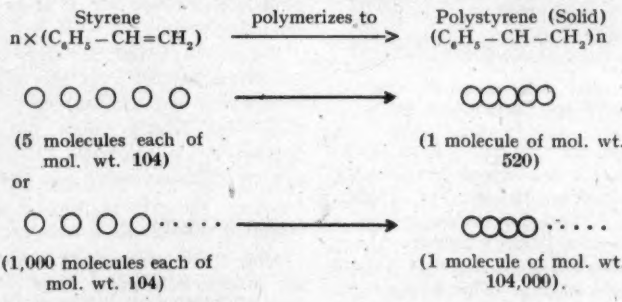
SO far we have dealt with those plastic materials the manufacture of which entails merely the use of natural substances such as bitumen and their mechanical manipulation, or the use of natural materials, e.g., protein or cotton, wood, etc., which are already made up of large molecules and need but a chemical reaction to change them into the plastic materials—casein, celluloid, cellulose acetate, etc. None of these plastics is called synthetic since this word is reserved for compounds which are built up from relatively simple chemicals of low molecular weight.

The sections of plastics now to be described are all synthetic, and we shall first describe those which, like the preceding ones, are thermo-plastic in character.

They are all members of what is called, in chemistry, the ethenoid or vinyl family of compounds, being theoretical derivatives of the gas ethylene $CH_2=CH_2$. The vinyl group is shown as $-CH=CH_2$ and derivatives of it as $R-CH=CH_2$ where R is symbolic of another chemical grouping.

All the synthetic ethenoid resins are derived from these simple derivatives called monomers by polymerization; that is, a number of monomers of low molecular weight combine to form a smaller number of polymers of high molecular weight.

To take a concrete but symbolic example in styrene, a colourless liquid boiling at 146 degrees C. with an aromatic odour and of molecular weight of 104. Polymerization takes place under the influence of sunlight, heat and the action of catalysts.



The above is merely diagrammatic.

By suitable control a polystyrene of any desired molecular weight can be obtained, although in actual practice a manufacturer puts on the market a small number, say, two or three polystyrenes of different molecular weight, e.g., 25,000 for moulding powders and a lower one, about 15,000, for making solutions for coating purposes. (Note: The higher the molecular weight the lower the solubility.)

The above notes also apply to the other polyvinyl compounds shown in the diagram on the opposite page. All may undergo grinding for production of moulding powders with or without pigments, admixture with plasticizers to allow ease of moulding, etc., extrusion and casting into tubes, rods, or sheets or tapes.

Polystyrene.—Pre-eminently suitable for electrical mouldings, sheets, tubes, etc. Trade names: Distrene (British), Styron, Bakelite (U.S.A.).

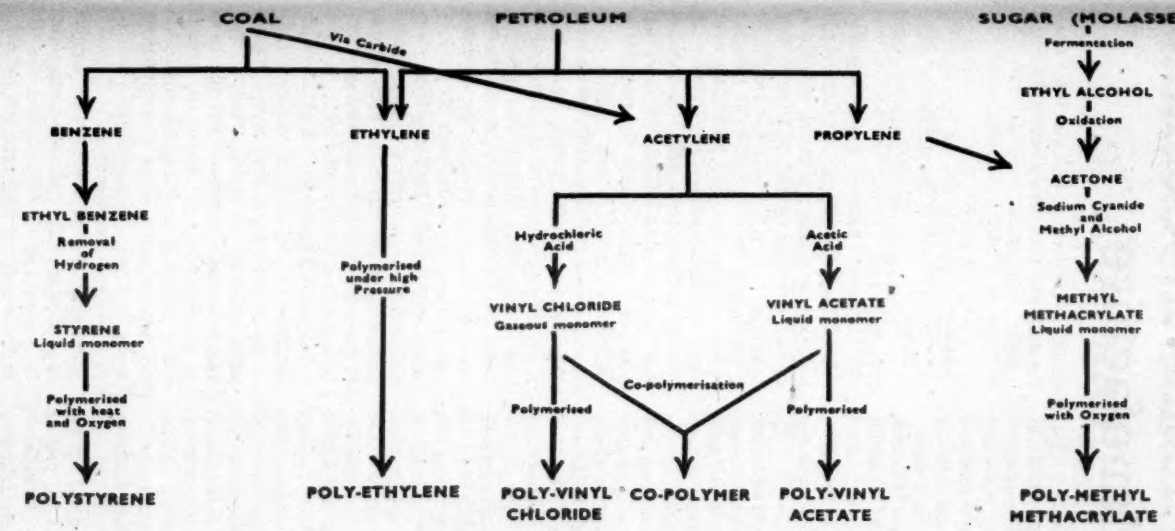
Polyethylene.—Tough and somewhat rubbery. Excellent for electrical films and tapes, bottle stoppers. Trade name: Alkathene (British).

Polyvinyl Chloride.—Tough and somewhat rubbery. Electrical sleevings. Trade names: Welvic and P.V.C. (British), Koroseal (U.S.A.).

Polyvinyl Acetate.—Excellent adhesive and for incorporation in lacquers, etc. Trade names: Geiva (Canadian), Vinylite (U.S.A.).

The co-polymer of vinyl chloride and acetate is tough, non-warping, and highly chemical resistant. Trade name: Vinylite and Vinyon (U.S.A.).

Polymethyl methacrylate.—Pre-eminent as organic glass in the sheet form. Powdered form as moulding material for electrical goods, etc. Trade names: Perspex and Diakon (British), Lucite (U.S.A.).



Mechanical and Physical Properties.

	Polystyrene	Polyethylene	Polyvinyl chloride	Polyvinyl acetate	Polymethyl methacrylate
Sp. gravity	1.04	0.95	1.35	1.2	1.18
Tensile strength (tons sq. in.)	3	—*	1.3	—	3-4
Impact strength (ft./lb.)	0.25-0.5	—*	0.6-1	—	0.3-0.5
Dielectric strength volts/mil.	600	—*	600	—	300-500
Vol. resistivity (ohm/cm.^{3})	10^{17}	—*	10^{13}	10^{13}	10^{14}
Power factor (10^6 cycles)	0.0002	—*	0.02	0.02	0.02

* Figures not yet made generally available. The electrical properties are stated to be excellent.

Synthetic Resins in Gelatine Manufacture

ONE of the most interesting and potentially important applications of synthetic resins in the gelatine industry is suggested in B.P. No. 521,646, taken out in 1940 by Dr. E. E. Jelley, Eastman Kodak. The specification deals with the purification of gelatine for use as a photographic base where complete freedom from calcium salts is essential to avoid precipitation of dyes to be incorporated in the gelatine base itself or in the silver halide emulsion. Purification can be effected in two definite phases:—

(1) Warm 10-20 per cent. gelatine aqueous solution passed through Zeolite filter to remove calcium salts and reduce ash to 0.2 per cent. or less.

(2) If the gelatine is contaminated with saline matter, e.g., chlorides, sulphates and so forth, these will be converted into acids and therefore the effluent from the filter may be passed through an acid-absorbing filter composed of a synthetic resin as described in B.P. 450,309.

It will be remembered that B.P. 450,309 was taken out in July, 1936, by Basil Adams and Eric L. Holmes, of the Chemical Research Laboratory, Teddington. The preamble to this specification states that " the products obtained by the action of aldehydes upon bodies containing one or more amino groups and bodies classified as albuminoids or proteins possess properties which render them suitable for use in absorbing particular constituents or components from solutions or gaseous mixtures and in particular in removing certain amines from solution and generally the replacement of the removed amine by another amine.

The resins obtained from aniline, m-toluidine, symmetrical-m-xylidene, m-phenylene-diamine, are specified by the inventors. Tests carried out by passing acid solutions (0.0035 N.) through 10 grammes of each resin give the following results in the form of volumes from which the acid was completely removed.

Resin obtained from	HCl. c.c.	HNO_3 c.c.	H_2SO_4 c.c.
Aniline ...	1,100	1,000	1,200
m-toluidine	2,500	1,500	2,000
Sym-m-xylidene	1,800	1,800	2,300
m-phenylene-diamine...	2,600	1,800	2,300

In the case of neutral salts, the results achieved by passing a dilute solution of sodium sulphate (0.0035 N.) are:—

Aniline	1,800 c.c.
m-toluidine	2,200 c.c.
Sym-m-xylidene	2,100 c.c.
m-phenylene-diamine ...	1,000 c.c.

B.P. 506,291 taken out by Permutit Co., Ltd., and others (Holmes and Prescott) carries the application of the above resins a step farther. The patent covers the preparation of resins as thin layers on carrier bodies, e.g., pumice is first impregnated with the amine, dried and subsequently treated with aldehyde.

By the joint use of suitable zeolites and synthetic resins to remove the objectionable anions, a gelatine can be produced suitable for the highest-grade photographic base, particularly for the manufacture of colour plates and films where it is essential that the minimum precipitation of dye should be effected.

In the manufacture of photographic gelatine it is desirable to employ distilled water or water containing a very low total solid content. Use of distilled water entails a costly and expensive plant, and it is, therefore, of interest to consider other means of purifying the water. By far the simplest method is to utilize two types of filter, (1) quebracho resin, (2) m-phenylene-diamine resin. Tap water containing 19 p.p. 100,000 can, by passing through the above resin filters, be purified to the extent that the total solids is reduced to 1 part per 100,000.

Comparative Burning Tests of Common Plastics

OWING to the increasing use of modern plastic material extensive burning tests were recently published by the Underwriter's Laboratories Inc., Chicago, U.S.A., carried out by A. J. Perkins, Ph.D. (Bulletin of Research, No. 22, August, 1941, New York). The laboratory is sponsored by the American National Board of Fire Underwriters. The object was to determine the comparative combustibility of some of the more commonly used plastics. Representations of the more important commercially produced plastics were investigated, including cellulose acetate, cellulose acetate butyrate, acrylate resins, polystyrene, polyvinyl alcohol, polyvinyl chloride, vinyl-chloride and acetate co-polymers, phenol formaldehyde, urea formaldehyde, casein, coumarone-indene and cold-moulded plastics.

In all 11 different plastics were tested in the form of slabs of different thickness, between $\frac{1}{16}$ in. to $\frac{1}{2}$ in., and lengths between 4 ins. to 6 ins., the widths being $\frac{1}{2}$ in. to 1 in.

The Plastics Under Test

The following American brands of plastics were employed for the test:—

Cellulose acetate: Tenite I and Fibestos.

Cellulose acetate butyrate: Tenite II.

Acrylic resins: Lucite and Plexiglas.

Polystyrene: Bakelite.

Polyvinyl alcohol: Resistoflex.

Phenol-formaldehyde: Opalon (cast resin), Resinox moulded from powder (cotton, wood and asbestos-filled).

Urea-formaldehyde: Plaskon and Beetle.

Casein: Ameroid.

Vinyl chloride-acetate co-polymers: Vinylite (plasticized and unplasticized).

Polyvinyl chloride: Koroseal.

Cold-moulded: Thermoplax.

(Note.—The American expression cold-moulded is generally applied to bituminous or inorganic refractory compounds. Presumably Thermoplax is an asbestos-filled bituminous plastic.)

Cellulose nitrate was omitted since its fire hazard is well known, the slow-burning cellulose acetate was however included for comparison purposes.

Method of Test

Information as to the relative ease of ignition, and a rough indication of the comparative burning rate of the specimens of various sizes and cross-section was desired. The relative ease of ignition was measured by the duration of application of a standardized test flame to the specimen necessary to cause ignition. The comparative burning rate was then indicated by the length of time the specimen burned. This may allow a general classification of the combustibility dependent on (1) the ease of ignition, and (2) the comparative burning rate. A quantitative classification of combustibility would further entail the determination of the ignition temperature and an exact comparison of the burning rates, as well as tests on larger samples, but this was outside of the scope of the present investigation.

Where the size of the samples permitted, a cross-section of the specimen of $\frac{1}{16}$ sq. in. was attempted so that burning times of equal volumes could be obtained. The test flame was a $\frac{3}{4}$-in. high luminous (yellow) gas flame, these dimensions being approximately the same as those of the flame of a common match. The specimens were hung vertically in an enclosure intended to prevent draughts, the test flame being applied to the lower end. The duration of application of the flame, the length of time that the specimen burned, and the height of flame, were recorded, and any after glow noted.

Table 1.—Specimens of Plastic Subjected to Burning Tests.

Plastic	Sample	Trade name	Thickness, in.	Colour	Fabrication	Nature	Remarks
Cellulose acetate	A	Tenite I	1/16	Red	Moulded	Thermoplastic	
	B	Tenite I	1/4	Grey	Moulded	Thermoplastic	
	C	Tenite I	1/4	Blue	Moulded	Thermoplastic	
	D	Tenite I	1/4	Amber	Moulded	Thermoplastic	
	E	Fibestos	1/4	Crystal	Moulded	Thermoplastic	
	F	Fibestos	1/4	Crystal	Moulded	Thermoplastic	
	G	Fibestos	1/4	White	Moulded	Thermoplastic	
	H	Fibestos	1/4	Red	Moulded	Thermoplastic	
Cellulose acetate butyrate	A	Tenite II	1/16	Clear	Moulded	Thermoplastic	
	B	Tenite II	1/4	Clear	Moulded	Thermoplastic	
Acrylate	A	Lucite	1/4	Clear	Moulded	Thermoplastic	
	B	Plexiglas	1/4	Clear	Cast	Thermoplastic	
Polystyrene		Bakelite Polystyrene	1/16	Clear	Moulded	Thermoplastic	
Polyvinyl alcohol	A	Resistoflex	1/16	Amber		Thermoplastic	
	B	Resistoflex	1/16	Amber		Thermoplastic	
Phenol-formaldehyde ..	A	Opalon	1/4	Yellow	Cast	Thermosetting	
	B	Resinox	1/4	Black	Moulded	Thermosetting	Cotton filled
	C	Resinox	1/4	Black	Moulded	Thermosetting	Wood filled
	D	Resinox	1/4	Black	Moulded	Thermosetting	Asbestos filled
Urea-formaldehyde ..	A	Plaskon	1/16	White	Moulded	Thermosetting	
	B	Beetle	1/4	Cream	Moulded	Thermosetting	
Casein	A	Ameroid	1/4	Pink	Moulded	Thermoplastic	
	B	Ameroid	1/4	Black	Moulded	Thermoplastic	
Vinyl-chloride	A	Vinylite	1/4	Clear	Moulded	Thermoplastic	} Plasticized
Vinyl-acetate	B	Vinylite	1/4	Clear	Moulded	Thermoplastic	
Copolymers	C	Vinylite	1/4	Clear	Moulded	Thermoplastic	
	D	Vinylite	1/4	Black	Moulded	Thermoplastic	} Unplasticized
	E	Vinylite	1/4	White	Moulded	Thermoplastic	
	F	Vinylite	1/4	Clear	Moulded	Thermoplastic	
Polyvinyl chloride		Koroseal	1/4	Black	Milled	Thermoplastic	Plasticized
Cold moulded		Thermoplax	1/4	Black	Moulded	Thermosetting	

Examination of Results

The results of tests, individually listed in the original report, can be divided into three groups. Group No. 1 includes those plastics which are ignited by the test flame in approximately the same time, and burn at about the same rate as cellulose acetate. Group No. 2 includes those plastics burning with a feeble flame which is extinguished by a slight draught and which may or may not propagate away from the point of ignition. Group No. 3 includes those plastics which burn only during the application of the test flame. Cellulose nitrate, among whose hazardous properties is that of exathermic decomposition, would fall into a group more hazardous than designated as No. 1.

For the plastics of Group 1 cellulose acetate was used as a standard. Seven of the eight individual compositions of cellulose acetate tested ignited within 10 secs. after the test flame had been applied and burned completely in from 3 to 5 mins. One specimen ($\frac{1}{4}$ in. thick and $\frac{1}{4}$ in. wide, Fibestos red) required a 15 secs. application of the test flame, but when ignited burned at about the same rate as the other compositions. Of other plastics the following had about the same ignition and burning times: cellulose acetate bufyrate, acrylate, polystyrene and one sample of polyvinyl alcohol.

With regard to plastics classified in Group 2 the following observations were made: The casein plastics were ignited rather easily, but burned for only a short time before being extinguished, the flame not being propagated to the

(Continued on page 238)

Table 2.—Results of Burning Tests.

Plastic	Sample	Group No.	Duration of applic. of test flame sec.	Duration of burning min.	Height of flame in.	Remarks
Cellulose acetate	A	1	4	5½	12	
	A	1	4	4½	12	
	B	1	10	3	8	
	C	1	7	4½	8	Specimens melted while burning, flaming drops falling to base of cabinet where they continued to burn
	D	1	10	3½	8	
	E	1	7	4½	7	
	F	1	10	3½	7	
	G	1	10	5½	7	
	H	1	15	6	6	
Cellulose acetate butyrate	A	1	10	10	8	Reignited several times, as burning portion fell off. Fallen material continued to burn, leaving a small amount of residue
	A	1	10	6	8	
	B	1	10	5	5	
Acrylate ..	A	1	5	3½	12	Burned completely, melted. Flaming drops fell to base of cabinet where they continued to burn
	A	1	5	05	12	
	B	1	5	5½	12	
Polystyrene ..	—	1	3	2½	4	Burned completely. Smoky flame. Melted. Flaming drops fell to base of cabinet where they continued to burn
	—	1	3	4½	4	
Polyvinyl alcohol	A	1	7	2½	5	Burned completely. Smoky flame. Melted
	A	1	7	3½	12	
	B	3	—	—	—	Burned only during application of test flame
	B	3	—	—	—	
Phenol-formaldehyde	A	2	60	½	3	Reignited three times. Charred residue remained
	B	2	60	20+	5	Flame propagated from bottom to top of specimen in about 5 mins. Specimen then continued to burn without flame
	B	2	30	18	5	
	C	2	60	1	2	Flame did not propagate the entire length of specimen. Afterglow
	C	2	30	2	2	
	D	3	—	—	—	Burned only during application of test flame
	D	3	—	—	—	
Urea-formaldehyde	A	2	90	9	2	Reignited several times. Flame blows off surface. Charred residue remains. Afterglow
	A	2	75	10	2	
	B	2	—	—	—	In vertical position, burned during application of test flame only. In horizontal position, burned for about one min. after a one-min. application of the test flame
Casein	A	2	30	2	2	Flame does not propagate away from heated area
	B	2	30	2	2	
Vinyl-chloride Vinyl-acetate copolymers	A	2	20	5½	3	Reignited several times. Flame blows off surface. Charred residue remains
	A	2	40	6	4	
	B	3	—	—	—	Burned only during application of test flame
	B	3	—	—	—	
	C	3	—	—	—	Burned only during application of test flame
	C	3	—	—	—	
	D	3	—	—	—	Burned only during application of test flame
	D	3	—	—	—	
	E	3	—	—	—	Burned only during application of test flame
	E	3	—	—	—	
	F	3	—	—	—	Burned only during application of test flame
	F	3	—	—	—	
Polyvinyl chloride	—	3	—	—	—	Burned only during application of test flame
Cold-moulded	—	3	—	—	—	Burned only during application of test flame
Coumaro-indene	Pellets		10	—	—	Burned with a smoky flame about 2 ins. high

[Editor's Note: Several readers have been puzzled by the inclusion, last month, of the trade name Bakelite in the polystyrene resins. It should be made clear that Bakelite is a trade name owned by the Bakelite Corporation, and is applied to more than one of its products. One of the polystyrenes included in Tables 1 and 2 is known under this trade name.]

Phenol-formaldehyde Plastics
Under Conditions of Bending Fatigue

With the increased use of plastics for stressed components in industry the need for data regarding their behaviour under stress is urgent. The following report is therefore of importance to both users and to the plastics industry

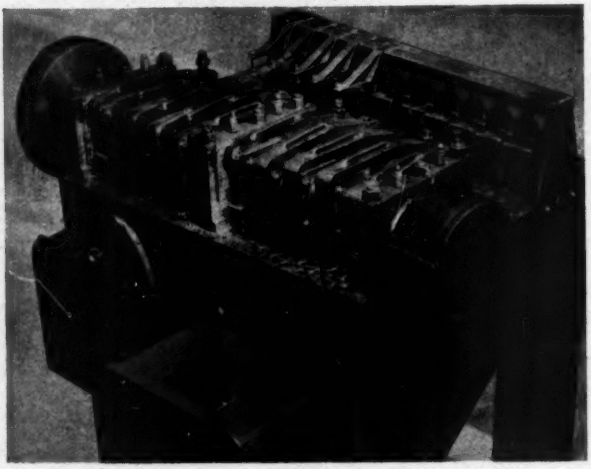
By
D. WARBURTON-BROWN,
A.M.I.A.E., M.I.P.I.

Summary of Results

Although the range of moulding materials tested had tensile strengths which varied from 5,500 lb./sq. in. to 30,000 lb./sq. in. and varied in type from pure unfilled phenol-formaldehyde resin to fabric base laminated material, the limiting stress for bending fatigue in all cases fell within the range of ± 1.95 to ± 2.40 tons/sq. in.

From this it is concluded that the type of reinforcement employed (i.e., the filler) has only limited influence upon the fatigue limit of this type of plastic. It does, however, influence the slope of the fatigue curves, and probably the fatigue "life" of the materials.

IN view of the lack of specific information regarding the behaviour of thermosetting plastics of the phenol-formaldehyde type, tests were carried out in order to determine approximate values of the limiting bending fatigue stress for a representative range of moulding materials made from these resins.



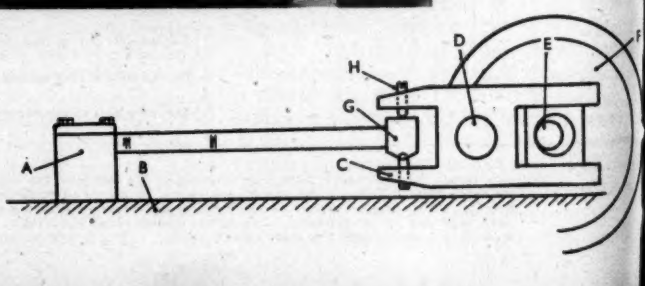


Plate 1 (above) and Fig. 1 (right).—General and detailed view of the bending fatigue machine.

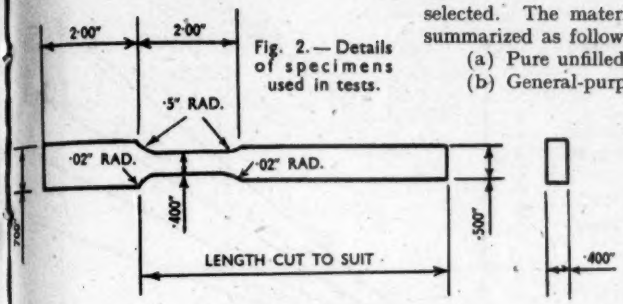


Fig. 2.—Details of specimens used in tests.

Plate 2.—Typical fracture in bending fatigue tests.

Introduction

Owing to the scarcity of information regarding the fatigue properties of phenol-formaldehyde moulding materials and the fact that this type of plastic is advocated for lightly stressed aircraft components, a series of bending fatigue tests were carried out with a view to determining the approximate value of the limiting alternating stress in bending for a representative range of materials of this type.

No attempt was made to obtain academic results and no special precautions were taken to control the temperature and humidity of the atmosphere during tests. The results obtained will, however, give a useful indication as to the permissible alternating bending stresses to which mouldings may be subjected.

The contents of this report deal with bending fatigue only, and a series of tension fatigue tests are to be run at a later date in order to obtain more complete information on the subject of the fatigue properties of plastics.

Range of Materials Tested

It is obviously impossible to carry out tests on all the various grades of p.f. moulding powders which are available, and for the purpose of the tests described in this report a representative range of moulding materials of this type were selected. The materials chosen may be summarized as follows:—

(a) Pure unfilled p.f. resin.
(b) General-purpose material.
(c) Semi-shock - resisting material.
(d) Paper base laminated material.
(e) Fabric base laminated material.

The unfilled resin was tested as a result of tests carried out on other grades which suggested that the type of reinforcement used had little effect upon the fatigue limit of the moulding. In practice, unfilled resin is not used owing to its extremely brittle nature.

Description of Apparatus

All tests outlined in this report were carried out on the bending fatigue machine which is shown diagrammatically in Fig. 1 and also in Plate 1.

Briefly, the machine consists of a series of ten clamps (A) (Fig. 1), which are secured to a base plate (B) at varying distances from a corresponding series of rocker arms (C) oscillating about a shaft (D) and actuated by eccentrics (E). The eccentrics have a throw of .100 in. and

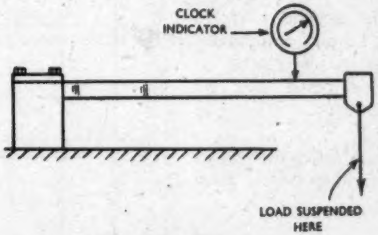


Fig. 3.—Method used for calibration of specimens.

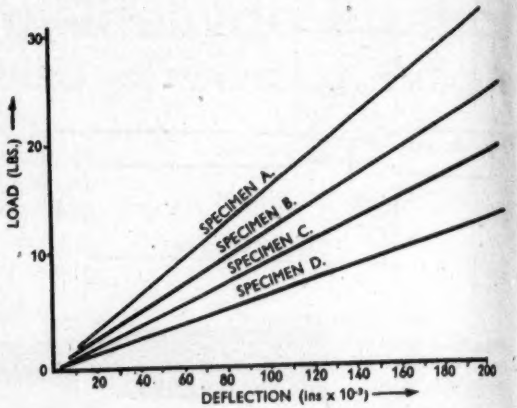


Fig. 4.—Typical specimen calibration curves.

are driven by an electric motor at a speed of 2,000 r.p.m. A flywheel (F) is fitted to one end of the eccentric shaft to absorb energy fluctuations.

The test pieces are secured at one end in the clamps (A). Metal saddles (G) are fitted over the free end and are located in the fork of the rocker arms by spherically ended bolts (H), which allow for the angular movement of the rockers.

Specimens were all made to details shown in Fig. 2, and in all cases were moulded, with the exception of fabric-laminated specimens, which were machined from sheet material. The length was made to suit the particular set of clamps and rockers in use.

Calibration of Specimens

In order that the value of the alternating stress in any specimen may be calculated it is first necessary to calibrate the specimen as described below:—

The specimen to be calibrated is clamped in the machine with the metal saddle (G) located in position over the free end of the cantilever. An arbitrary point is marked along the length of the specimen and a clock indicator gauge is placed at this point and set to zero. (See Fig. 3.)

A series of weights is suspended from the saddle, and the corresponding deflections of the specimen noted. From this information a load/deflection curve is drawn for the specimen. A typical set of load/deflection curves is shown in Fig. 4.

The saddle (G) is then located on the spherical bolts, which are so adjusted that upon turning the eccentric equal deflections occur each side of the centre line of the specimen.

With the clock indicator in the same position the eccentric shaft is rotated and the maximum deflection noted. From the load/deflection curve already prepared for the specimen the corresponding load

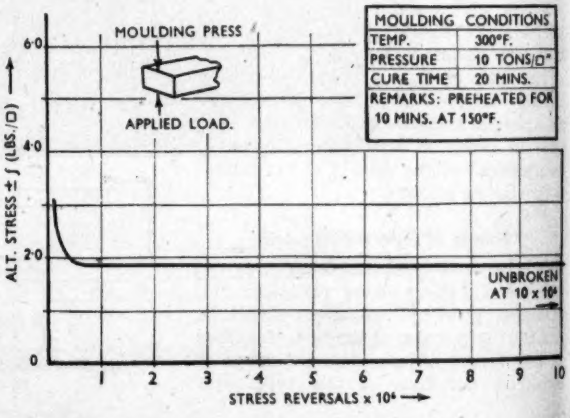


Fig. 5.—Bending fatigue curve for unfilled P.F. resin.

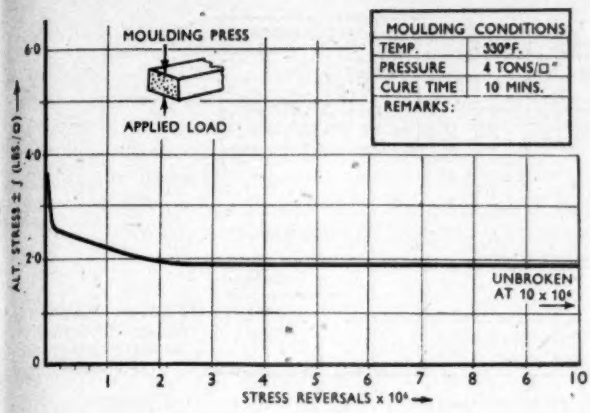


Fig. 6.—Bending fatigue curve for woodflour-filled P.F. resin.

can be obtained, and, since the length of the specimen can be measured, the value of bending moment can be calculated.

The above procedure is carried out for each specimen to be tested.

Method of Determining Stress in Specimens

The value of the bending moment in any specimen having been obtained in the manner described, the value of the alternating stress in the specimen may be determined from the relationship:—

$$f = \frac{BM}{Z}$$

where f = stress.
BM = bending moment.
Z = section modulus of specimen.

For the type of specimens tested the value of Z is computed from

$$Z = \frac{bh^3}{6}$$

$$= \frac{.4 \times .4^2}{6}$$

$$= .0106 \text{ in.}^3 \text{ units.}$$

Since this value remains constant for all specimens and the bending moments can be calculated, it is possible to arrive at the alternating stress for each specimen under test.

Test Results

In all cases four or five specimens were tested at stresses ranging from approximately ± 5 tons/sq. in. to ± 1.90 tons/sq. in.

For the purpose of the present tests the

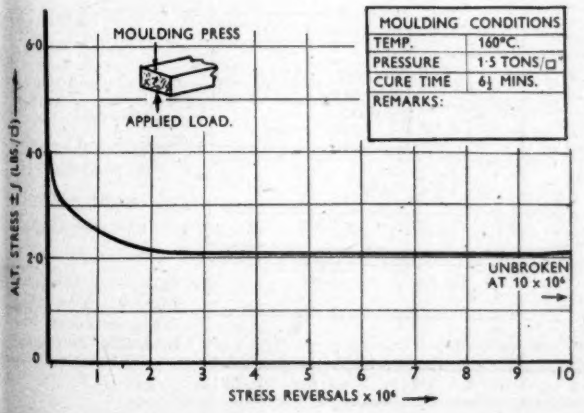


Fig. 7.—Bending fatigue curve for cellulose fibre-filled P.F. resin.

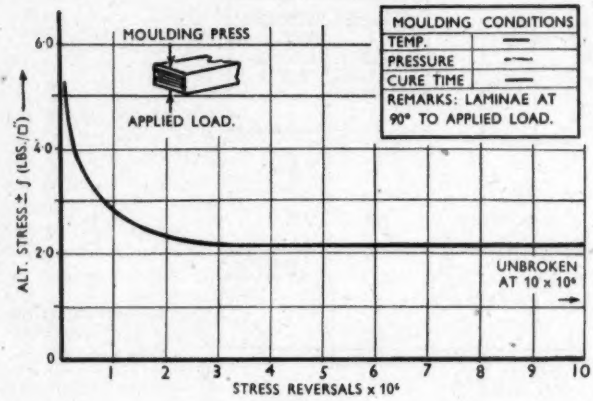


Fig. 8.—Bending fatigue curve for laminated paper-base P.F. resin.

fatigue limit was determined as that stress at which the specimen remained unbroken after 10 million stress reversals. It is possible that the figures are a little high, since the material may not withstand a greater number of reversals at the same stress, but 10 millions is considered to constitute a fairly good " life."

The results for the range of materials tested are set out in Tables 1 to 5 and are plotted in Figs. 5 to 10. Table 6 compares the tensile and fatigue values of the materials tested.

It will be seen that the fatigue limit for the complete range of plastics tested falls within the range of ± 1.95 to ± 2.40 tons/sq. in. Comparative curves are plotted in Fig. 11.

The tensile strengths of the materials under review are compared in Fig. 12, from which it will be seen that these vary from 5,500 lb./sq. in. to 30,000 lb./sq. in. —that is a variation of approximately 80 per cent. in the tensile strength is made possible by the introduction of reinforcing fillers. It is interesting to note that these fillers result in an increase of only 18 per cent. in the bending fatigue limit.

The explanation for this can be found if the moulding is regarded as a resin/filler mixture in which the resin will be

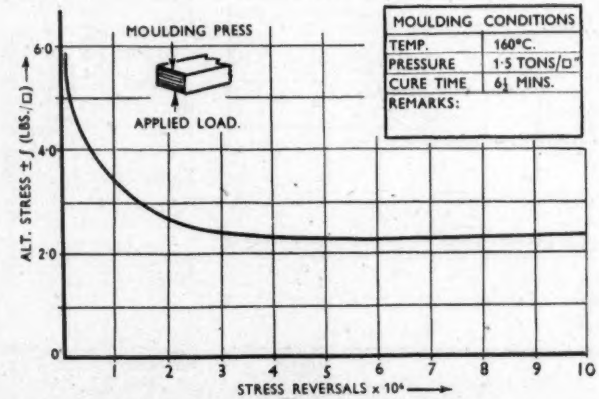


Fig. 9.—Bending fatigue curve for laminated fabric-base P.F. resin.

Table 1.—Bending Fatigue Properties of Unfilled P.F. Resin.

Specimen	Alternating stress	Reversals to failure
A	±2.60 tons/sq. in.	Almost instantaneous
B	±2.40 tons/sq. in.	60,000
C	±1.98 tons/sq. in.	400,000
D	±1.93 tons/sq. in.	Unbroken at 10×10^6

Table 2.—Bending Fatigue Properties of Woodflour-filled P.F. Resin.

Specimen	Alternating stress	Reversals to fracture
A	±3.45 tons/sq. in.	20,000
B	±2.85 tons/sq. in.	40,000
C	±2.55 tons/sq. in.	70,000
D	±2.45 tons/sq. in.	440,000
E	±1.96 tons/sq. in.	Unbroken at 10×10^6

Table 3.—Bending Fatigue Properties of Cellulose Fibre-filled P.F. Resin.

Specimen	Alternating stress	Reversals to fracture
A	±4.75 tons/sq. in.	Almost instantaneous
B	±3.15 tons/sq. in.	240,000
C	±2.80 tons/sq. in.	720,000
D	±2.05 tons/sq. in.	Unbroken at 10×10^6

Table 4.—Bending Fatigue Properties of P.F. Resin with Paper Laminations.

Specimen	Alternating stress	Reversals to fracture
A	±5.05 tons/sq. in.	136,000
B	±3.31 tons/sq. in.	630,000
C	±2.20 tons/sq. in.	Unbroken at 10×10^6

Table 5.—Bending Fatigue Properties of Laminated Fabric Base P.F. Resin.

Specimen	Alternating stress	Reversals to fracture
A	±4.9 tons/sq. in.	50,000
B	±2.58 tons/sq. in.	925,000
C	±2.46 tons/sq. in.	4,800,000
D	±2.40 tons/sq. in.	Unbroken at 10×10^6

Table 6.

Material	Tensile strength (tons/sq. in.)	Specific gravity	Specific tensile strength (tons/sq. in.)	Bending fatigue limit (tons/sq. in.)	Specific fatigue limit (tons/sq. in.)
Pure resin (unfilled)..	3.5	1.27	2.75	±1.93	±1.52
Woodflour-filled p.f. resin ..	3.0	1.35	2.20	±1.96	±1.45
Cellulose fibre-filled p.f. resin ..	3.5	1.35	2.58	±2.05	±1.52
Paper base laminated p.f. material	12.5	1.40	8.09	±2.20	±1.57
Fabric base laminated p.f. resin ..	8.0	1.36	5.09	±2.40	±1.75

Tables 1 to 5 give the individual bending fatigue properties of the five different types of phenol-formaldehyde plastic materials under the prescribed tests. Table 6 gives their comparative physical and mechanical properties, including their fatigue limits.

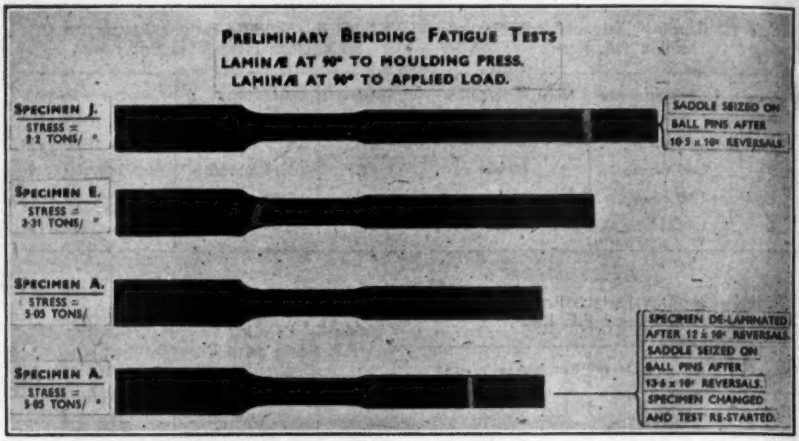

PRELIMINARY BENDING FATIGUE TESTS
LAMINÆ AT 90° TO MOULDING PRESS.
LAMINÆ AT 90° TO APPLIED LOAD.
SPECIMEN J.
STRESS = 2·2 TONS/
SADDLE SEIZED ON BALL PINS AFTER 10·5 x 10⁶ REVERSALS.
SPECIMEN E.
STRESS = 3·31 TONS/
SPECIMEN A.
STRESS = 5·05 TONS/
SPECIMEN A.
STRESS = 5·05 TONS/
SPECIMEN DE-LAMINATED AFTER 12 x 10⁶ REVERSALS.
SADDLE SEIZED ON BALL PINS AFTER 13·6 x 10⁶ REVERSALS.
SPECIMEN CHANGED AND TEST RE-STARTED.

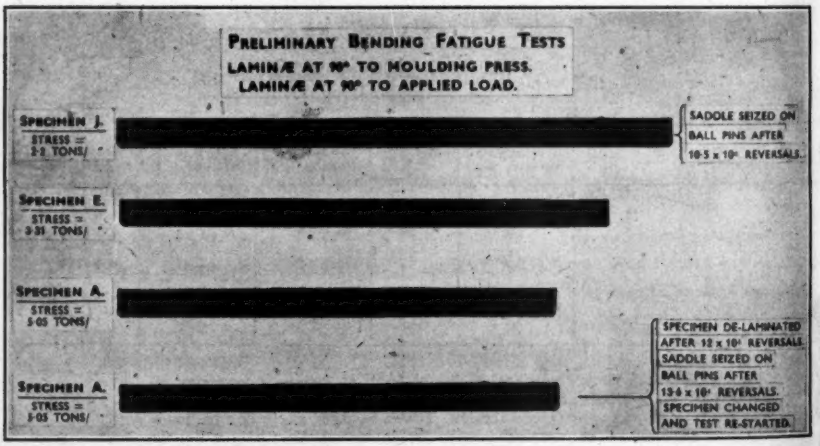
Plate 3 above) and Plate 4 (below) demonstrate the appearance of laminated specimens, in top and side views, on undergoing bending-fatigue tests under varying stresses.

Fig. 10 (right) shows the local swelling in—

—laminated specimens due to delamination.

the weak link owing to its extremely brittle nature.

When a moulded test specimen is subjected to bending the resin surface skin is subjected to the heaviest stress, and if this exceeds a certain value a crack will


PRELIMINARY BENDING FATIGUE TESTS
LAMINÆ AT 90° TO MOULDING PRESS.
LAMINÆ AT 90° TO APPLIED LOAD.
SPECIMEN J.
STRESS = 2·2 TONS/
SADDLE SEIZED ON BALL PINS AFTER 10·5 x 10⁶ REVERSALS.
SPECIMEN E.
STRESS = 3·31 TONS/
SPECIMEN A.
STRESS = 5·05 TONS/
SPECIMEN A.
STRESS = 5·05 TONS/
SPECIMEN DE-LAMINATED AFTER 12 x 10⁶ REVERSALS.
SADDLE SEIZED ON BALL PINS AFTER 13·6 x 10⁶ REVERSALS.
SPECIMEN CHANGED AND TEST RE-STARTED.

develop in the resin and the fatigue limit referred to in this report is based on the appearance of the first surface crack on the surface of the specimen.

The curves in Fig. 11 indicate that, although there is little difference in the value of the limiting stress for the various types of mouldings tested, those which have fibre or laminated fillers take a greater number of reversals to reach the limiting value than is the case with the pure resin or the woodflour-filled material.

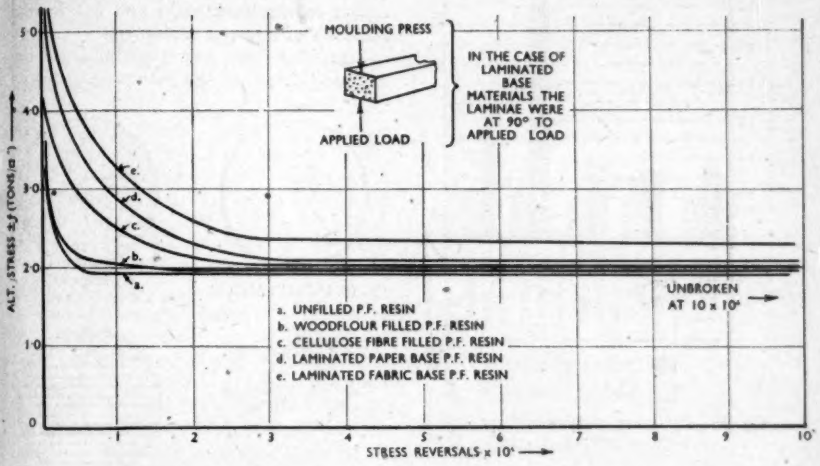


Fig. 11.—Comparative bending fatigue curves for various phenolic materials.

Fig. 13 illustrates diagrammatically sections through the four main types of material tested, and will help to explain the reason for the longer period required to reach the fatigue limit in the case of the more heavily reinforced materials.

In the case of the pure unfilled p.f. resin, Fig. 13 (a), when a crack forms on the surface there is nothing to restrict the propagation of the crack, hence it spreads through the material quickly. In the case of the woodflour-filled moulding, the rate of progress of the crack is retarded slightly since it must work round each particle of woodflour which lies in its path.

With the fibrous fillers the retardation is even greater owing to the numerous small interlocked fibres which must be circumvented by the crack. The resistance of laminated materials to the propagation of cracks is even greater since the crack must pass through a highly compressed mass of interlocked fibres.

Types of Fracture

In the case of all materials except those of the laminated type, the fractures, which all occurred at a point approximately the position of maximum stress, were of an irregular nature and little could be learned from examination of the cracks. A typical example of a non-laminated failure is shown in Plate II. The specimen shown is in a cellulose fibre filled material.

The case of the laminated materials is somewhat different however, since the specimens were considered to be fractured with the appearance of the first surface crack. The more highly stressed specimens were, however, run up to the limit of 10 million stress reversals before being removed from the machine.

It was decided to take the fatigue limit as the point at which the first surface

cracks appeared because the high resistance to the propagation of cracks in laminated materials enables considerable running to be carried out after the initial breakdown of the material. Also once the fatigue crack has started the material will be weaker in other respects—e.g., tension; and in practical applications it is unlikely that moulded components will be in pure bending.

It was observed that cracks in

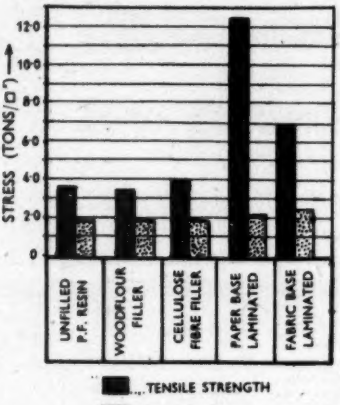


Fig. 12.—Influence of type of filler on physical properties.

laminated specimens were preceded by a local lightening in colour of the surface. As the breakdown of the laminæ proceeded, the specimen delaminated locally and a swelling occurred at the points of maximum stress. (See Fig. 10.) Typical failures of laminated specimens are shown in Plates III and IV.

Conclusions

The range of materials covered by the series of tests described in this report is fairly representative of the phenol-formaldehyde materials used in engineering applications.

The materials all have a p.f. resin for the base and differ in the type of reinforcing filler which is used. The influence of the filler on the physical properties of the final moulding is considerable, as can be seen (in the case of tensile strength) from Fig. 12. From this chart it will be observed that the tensile strengths vary from 5,500 lb./sq. in. to as much as 30,000 lb./sq. in.

It is apparent, however, that the filler has comparatively little influence on the bending fatigue limit of these moulding materials, since in all cases this lies in the region of ± 1.95 to ± 2.40 tons/sq. in. Hence it would seem that any improvement in the fatigue properties of p.f. materials must be achieved by improvements to the basic resin and not by the addition of stronger fillers.

The filler does, however, influence the fatigue " life " of the moulding owing to

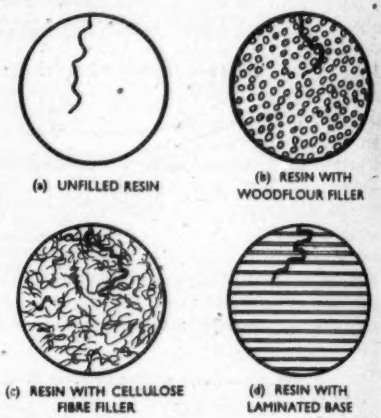


Fig. 13.—Propagation of cracks in various types of materials.

the varying degree of resistance offered to crack propagation.

Appendix

A secondary test was run at the conclusion of those described above in order to determine what the allowable alternating stress value was if the test was run up to 50×10^6 reversals.

An unfilled p.f. resin specimen was used and it was found that this was still unbroken at 50×10^6 reversals when the value of the alternating bending stress was ± 1.60 tons/sq. in.

World's Industry Employs Plastics

AIRCRAFT

Bomb components require, according to McBride (Industrial Service Research and Engineering Office, Chief of Ordnance, U.S. Army), special properties which plastics, at present, are only in part able to meet. Fuses and certain parts of fuses are a case in point. Here, where high shatter strength is required, it has so far not been found possible to use plastics. Nevertheless, for other fuse components it has been found possible to use impregnated paper, which has been found sufficiently inert to enable bursting charges to be stored with safety for long periods. **Bases for flares** have been produced in phenolics of high impact strength. Allied to these uses and, in part, directly applicable to aircraft, are shell parts, some of which have proved successful, but others of which have, so far, failed, due, it appears, either to lack of elasticity in the plastic or to the high thermal expansivity of plastics as compared with metals. **Grips and handles of guns and weapons of other types** have, according to McBride, been successfully produced as phenolic mouldings, at a cost no greater than that of the standard walnut pattern. **Bayonet scabbards** have been produced in a cotton material impregnated with cellulose acetate-butyrate. **Brush holders, spark plug connectors, terminal boards** and other components in aircraft electrical systems are, according to Willcox (Plastics Division, G.E.C.), writing in " Modern Plastics," now being injection moulded in Mycalex. The author of the account discusses rules for design in this new material and presents tabular data as to its physical, mechanical and electrical properties. Composed of glass-bonded ground mica, the S.G. of Mycalex varies between 2.95 and 3.44, and is made in various grades for different purposes. Particular attention is called to its low water absorption, namely, 0.003 per cent. for 48 hours' immersion in the case of a pressure-moulded grade for radio work, with a corresponding heat-resistance figure for the same grade of 325 degrees C. Thermal expansivity per degree C. is $8 \times 10 - 6$; tensile strength varies between 2-3 tons/sq. in.

MOTORS

Small cup-like mouldings in cellulose acetate have been developed by the Anti-Rust Corporation of U.S.A., and moulded by Caldwell Products Inc., to facilitate removal of rusted-in cylinder-head studs. The cups have moulded-in threads, by which they are screwed over the projecting stud. Into the enclosed area thus provided a rust-removing solution is poured from a container. Small holes around the base of the cup carry the fluid to the thread, whence it penetrates the rust deposit causing seizing. The particular solution used in conjunction with this fitting is stated to effect loosening in about 30 mins. Apropos of this point, it may be noted that, according to D.R.P. 523,071, methyl cyclohexanone possesses unique rust-softening properties. **Tanks and Armoured Cars** provide many obvious uses for thermo-setting mouldings of reasonable impact strength. Such uses are being extensively investigated

in U.S.A. The use of plastic bonded laminated wood and canvas for fans and motor clutch flywheels is particularly interesting, more especially as they are envisaged as replacing aluminium in this connection. **Fabric-based laminated phenolic material** is attracting special attention, although the water-absorbing qualities of the material are still causing trouble. **Thermoplastic Injection Mouldings** it appears, are coming in for consideration to replace light alloys for handles, control wheels, and similar components. McBride pays particular attention to the wide range of plastic materials and mechanical properties available to meet specific military needs.

SHIPBUILDING

Stern Tube Bearings in laminated phenolic material are discussed by Irvin, in the April issue of "Modern Plastics." They are employed in the form of semi-cylindrical segments, and, over long periods of service, have shown themselves entirely unaffected by highly polluted inland and inshore waters. Although this application is not new, the shipping drive in U.S.A. has drawn renewed attention to it.

CHEMICAL

Water-meter discs for use in hot water in various plastics, graphite and hard rubber were subjected to a comparative study, the results of which are presented in a recent account by Piper of the Detroit Edison Co. Phenolic resins with various fillers and a thermoplastic of high softening point were among the materials examined. The phenolics appear to be the most satisfactory, resisting deformation by water absorption or plastic flow even at 100 degrees C. Discs in these materials can be made to the fine limits required and previous experience has shown that they do not induce corrosion in neighbouring metal parts. **Corrosion-resistant flexible films** of polyisobutylene and certain soft rubbers extensively employed for lining chemical apparatus are limited in their use in so far as the layer is first caused to swell and may later be dissolved off by compounds containing benzene and certain alloys and greases. So, in degreasing plant, it has hitherto been customary to employ lead-lined containers where any degree of corrosion protection is required. According to Hinrich (abstracted in "V.D.I. Zeitschrift, 1942/86/No. 15-16), the initial swelling of suitable rubbers and polyisobutylenes may be prevented in such cases by pre-stressing the lining. Hinrich points out that by the inhibition of swelling in these materials, considerably increased resistance to dissolution by solvents is obtained. Pre-stressing is effected by the use of arched plates, the lining itself being strongly cemented to a very rigid base. Should any porosity or hair-cracking occur, slight swelling which does take place itself acts as an effectual seal. The author also notes that other chemically resistant materials frequently used for lining tanks in chemical work, such as bitumens and pitches, are taken up by solvents without swelling. **War-time chemical factories** and those allied to the chemical industry have so grown in number in Great Britain that the application of plastics for corrosion-resisting purposes has also increased apace. There is a wider use of asbestos-filled phenolic resins in the building of pickling tanks using sulphuric acid for the cleaning of metal sheet, and increased application of sprayed phenolics for the lining of tanks and tank-cars transporting chemicals. The rubber shortage has also enforced the examination of synthetics for the lining of hydrochloric-acid tanks.

FANCY GOODS

Vacuum containers for heated food and drink are playing an increasing part in war-time organization at home and in the field. Lids for such containers justly rank as heavy duty parts, and recently the Knapp Monach Co. (U.S.A.) have produced a jug of this type, in which the closure consists of a Durez moulding 1 in. deep and 3-in. dia. The manufacturers point out that this is both tasteless and odourless, and is designed expressly to stand rough service. **Metal economy** to the extent of 200 tons of brass rod per annum is represented by the substitution of Nixonite (cellulose-acetate plastic) for the tips of propelling pencils manufactured by Salz Bros., U.S.A.

FURNITURE

Card Indexing system developed by Visible Index Corp. embodies various types of plastics in the form of variously coloured extruded strips for handrails, top and bottom strips and index tabs. In this way sorting of information is greatly facilitated. **Furniture in factories, works canteens and military establishments** in U.S.A. appears likely to be benefited by pioneer work in the use of laminated wood for civil purposes of this nature developed for peace-time uses. In the special environments in which such furniture is employed, preservation of neat appearance with minimum upkeep is essential; durability and general sanitary considerations further call for the use of materials other than plain wood. Resin-bonded plywood amply meets all requirements.

MISCELLANEOUS

Wheels for the Lewis Shepherd hoist truck are now being moulded in phenolic-impregnated fabric. They are made in sizes ranging from 3-in. to 12-in. dia. and are finding extensive use in the chemical industries by reason of their resistance to attack by alkaline and acid chemicals. **Tin plate is substituted by cellulose acetate** in the new transparent kitchen scrapers marked by the Renewal Manufacturing Co. This somewhat unusual use of a synthetic resin demonstrates its ability to withstand an equally unusual type of wear. The new scraper is more artistic, more hygienic and more permanent than the former article made in metal. **Hollow tablet production** by means of a press is claimed in D.R.P. 707,612 (Hans Blache, Berlin). The process described is stated to be particularly useful for fibre-filled plastic masses. When the die has been filled with powder and the punch is just on the point of affecting compression, air is conducted through the punch in such a way that the resin and filler charge is distributed in the die cavity around a central air space. **Fermentation butyric acid,** according to Chem. Ind. Gemeinshaft, 1942/65/118, is attracting increased interest in Germany. Wood waste, leaves and straw are subjected to attack under carefully controlled conditions by prepared cultures of fermenting organisms. **Special thermocouple** for determination of interior temperature of rubber masses, more particularly car tyres, has been developed by the automobile research section of the Technical University of Stuttgart. It would appear that this instrument should be applicable for investigations upon rubber-like plastic masses with high internal damping capacity. It is characteristic of such materials that, as a result of energy absorption, interior temperatures of a high order may be reached.

Some Recent Developments in Du Pont Plastics

AMONG the leading producers of plastics in the United States of America is E. I. Du Pont de Nemours and Company, Inc., which operates several large plants devoted to the production and some to the fabrication of plastics. As, it is understood, the company exchanges information with Imperial Chemical Industries, Ltd., its operations should be of special interest to British users of plastics, since developments resulting from Du Pont research are, or are likely to be, made use of in England. A new laboratory building devoted to plastic research was opened last October at the Arlington, N.J., plant of Du Pont, and was dedicated to Dr. Allan F. Odell, who directed research from 1929 until his death in 1937.

Cellulose Plastics

Oldest of the Du Pont plastics is the nitro-cellulose plastic, Pyralin. One of the newer uses of this material is in hammer heads said to outlast wood, rubber, fibre and other mallets used in working metals. Pyralin, produced in sheets, rods and extruded tubes, continues in use for most of the extensive applications in which it has been employed.

Du Pont's cellulose acetate, Plastacele, although not dating so far back as Pyralin, has gained very wide use, not only in sheet form but in moulding compounds used in great volume in injection mouldings. A large production goes into automobile, aircraft, radio, and similar applications for knobs, escutcheons, dials, and a long list of other uses. There are sometimes as many as 60 applications of plastic in a single radio set, not all cellulose acetate, of course. Louverglas, already described in "Plastics," is among comparatively new uses of Plastacele. It is also extensively used to coat window screening to form a product called Cell-o-glas, which is translucent and transmits ultra violet light. It is widely used for windows in hen-coops and in horticulture, because it transmits the ultra violet rays which promote growth and are healthful to all life. As the material is flexible and not friable, it would seem to have possibilities for use where bombing raids are anticipated.

Methyl Methacrylate

Perhaps the fastest growing, though one of the most expensive of plastics produced in large quantities is the methyl-methacrylate Du Pont plastic, Lucite, produced in both cast and moulding forms. Although among the newer of the important plastics, it is finding extremely wide use, because of its clarity, ability to "pipe" light, unusual beauty and other factors. Probably the largest use is for windows and other transparent enclosures for aircraft where light weight, high clarity and ability to stand up in exterior exposure, along with non-shattering characteristics and ease of working are important considerations. The cast form is most used for these applications, as it has highest clarity and affords substantially perfect vision. Despite the extent of this use, supplies have been available for numerous industrial and decorative jobs.

Lucite has found wide use for lenses and for exterior ornaments in motorcars; for refrigerator parts, in which high resistance to moisture is required; or for radio applications in which beauty and transparency are desired, sometimes along with good dielectric properties; and for scores of home and commercial uses. Radio parts include dials, crystals, escutcheons and knobs. In refrigerators, crisper tray parts, defroster parts, evaporator doors, meat-keeper parts and the like are made from Lucite. Store displays require much of the same material and display models of automobile models, boats and many other products have been made largely from Lucite. Many pieces

of furniture have been produced largely or wholly from this acrylic plastic, as have many articles for home decoration and utility. Complete radio cabinets, and even piano cases, are among musical instrument components produced from Lucite. Other applications to musical instruments include chin rests for violins, saxophone mouthpieces, clarinets and reeds for wind instruments. Batons for conductors of orchestras, some involving "piped" light, are popular.

Industrial uses include sight feeds for lubricants, gauges of various types, parts for water chlorination, parts having contact with acids and other chemicals, markers, numbers and letters for highway and similar purposes, parts for fluorescent lighting equipment; conveyor aprons made from rod, to attain light weight; and the like.

An extremely large use of Lucite has developed in the brush- and toilet-ware industry. Hair brushes, clothes brushes, and hand brushes having Lucite backs are finding a wide sale because of transparency, natural beauty, strength, resistance to water and sanitary qualities. Combs, hand mirrors, cream jars, nail-file handles, and the like in clear and coloured transparencies are exceedingly popular and bring good prices.

Decorative uses are legion. They include costume jewelry, vases, candelabra, bowls, flowers, trays, tableware, picture frames, cosmetic containers, clock cases, desk accessories, and numerous ornamental pieces. Hardware for glass doors, parts for diathermy machines and electrostatic generators, "wrist-action" electrical plugs, tongue depressors, flashlight lenses, and smokers' accessories are among uses which combine utility with fine appearance and other saleable features. Some of the above, among other items, constitute "Bundles for Britain" merchandise finding wide sale.

The Newest Plastic

Although nylon is definitely a plastic, its primary use thus far has been, of course, in the hosiery industry, where it has taken the place of silk in large measure. There is, however, an extensive use in filaments of much larger diameter, perhaps the most important being in bristles for brushes, including, of course, tooth, hair, hand and clothes brushes, but also a great variety of brushes for industrial use where strength, high resistance to water and to chemicals are of great importance. Such brushes withstand prolonged soaking and abrasion, not to mention continued flexing. Life is said to range from two to twelve or more times that of natural bristle brushes. Industrial applications include many in breweries for washing and labelling, "furnisher" brushes used in fabric printing, many brushes used in dry-cleaning, brushes for removing refuse from sewage screens, brushes for vacuum cleaners, brushes for washing bottles and other equipment in the

American scene: Boat made of Lucite (methyl methacrylate resin) for display purposes.

dairy industry; brushes used in electroplating solutions, many of which are highly corrosive; and "edging" brushes used in the porcelain enamel industry. Nylon bristles come in diameters of 0.005 to 0.022 in. and have a tensile strength of 50,000 p.s.i., approximating to that of mild steel.

That nylon makes exceedingly strong filaments for such uses as strings for tennis and badminton racquets is now well known in the U.S.A. The author has used a tennis racquet strung with nylon for a full season, playing on numerous different types of surface an average of three times a week for about nine months, and the strings show no visible wear and appear to be as tight as when strung. Even playing in the rain or on a wet court has no effect. Other sporting uses include fishing leaders, which are exceedingly strong, can be tied and cast dry, do not fray and are practically invisible in water. Fish hooks snelled with nylon are now being produced and are displacing imported gut from Spanish silkworm sources. Brushes for gun-cleaning are also in extensive use. Surgical sutures of nylon have been in use for some time.

New World Variety

Another Du Pont plastic which has found a very wide use, yet is seldom seen by the user, is Butacite, a poly-vinyl acetal resin made in sheet form. Its chief application is as the sandwiched plastic in laminated glass, which has great strength and retains this strength and impact resistance in much greater degree at low temperatures than did the acetate sheeting previously used. The material is highly transparent, requires no cementing, is highly resistant to moisture, and is so flexible that a thin sheet will support the weight of a man, although the sheet stretches much like rubber. The same, or a very similar, material can be used for braces, belts, garters, wrist-watch bands, parts for shoes, and the like, and is likely to find more such uses now that American war needs have greatly reduced the requirements for laminated glass. Application in dielectric coverings for electrical conductors may come about, as similar vinyl compounds are now so used for wiring which is exposed to oil.

Du Pont originated and is making in greatly increased quantities the synthetic rubber known as neoprene. A large new plant has been erected recently for such production and a new type of great potential value to the automobile and aircraft industry was announced last September. All the neoprenes are resistant to lubricants and petroleum fuels, and have other properties which make them greatly superior to natural rubber for some purposes. Until recently, all known types of synthetic rubber have become hard and brittle at sub-zero temperatures, but the new Type FR neoprene is as "freeze-resistant" as natural rubber, according to Du Pont chemists. All neoprene, in common with other synthetic rubbers, costs more than natural rubber, but it has found wide use in many applications in which natural rubber has not been satisfactory or is inferior in performance characteristics. Recent tests in a simple part, the ordinary bib or water faucet washer, have shown those of neoprene to be much superior to the best natural rubber washer and to have much longer life. There are, of course, many highly important military and naval uses of neoprene, and the entire output is now subject to priorities which limit applications largely, if not wholly, to war needs. Industrial uses, however, include, or have included, printing press rolls.

The extent to which plastics of different types enter into much-used products, such as the typewriter, for example, gives some idea as to their utility and extent of use. The draw-string may be nylon, the platens neoprene (or Lucite, in the case of illuminated rolls for cutting mimeograph stencils), and knobs and keys may be Plastacele or Pyralin. Perhaps no one typewriter will use all these materials, but all are, or have been, employed for the purposes indicated and for other typewriter parts not named. Clearly, some highly important products have come from Du Pont test-tubes to fill the growing need for plastics.

while spending a million or so on a so-called un-economic synthetic rubber factory.]

I regret that I did not read into your Editorial the implied meaning suggested in your later comments and their implication now does not by-pass the commercial facts.

Carbide before the war was not a vital economic issue calling for State subsidy. The co-polymerized products of acetylene and their modification had special technical applications only, and so long as rubber was 12 times cheaper, possessed better rough usage properties, and held the commercial field, the plasticized acetylene derivatives were outpriced and, therefore, their employment restricted.

The acetylene field of chemistry has indeed been productive of spectacular results, and there are very powerful commercial interests in this country whose very existence depends upon a free and uninterrupted supply of carbide. The manufacture must of necessity, therefore, have received their careful investigation and could only have been abandoned on account of some inherent difficulties.

In support of your carbide claims, however, I believe I did exert that influence which eventually promoted the manufacture of polyvinyl chloride in this country.

Because Norway, Malaya and the East Indies have been overrun by the enemy and nine-tenths of the world's rubber supplies denied our use, is surely no reproof. To suggest that our legislators have been remiss in not anticipating such an event and subsidizing in advance of the war the erection of calcium carbide plants is not really thinking straight—not in our wildest dreams was misfortune such as this remotely contemplated.

The facts are that we were badly served by our legislators: a strong hand shown at the time against the Japanese invasion of Manchuria, coupled with American aid (which was offered then) would have had the effect of summarily ejecting the aggressor from China. Had that policy been adopted, together with sanctions in respect to scrap and petroleum, its influence for peace might have been far-reaching. If not wholly so, then the Far East certainly would have been spared the economic ravages of the invader.

I believe the future of synthetic compressible and recoverable products, together with their resins, is to be found in our richest mineral, namely, coal, and that the chlorination of acetylene is the longest way to the nearest point.

Nylon, of which we have only a flirting acquaintance, is, I believe, predestined to shape the future of plastics in a really big way. The basic constituent—adipic acid—is derived from coal. I believe the whole future of the Plastic Trade, as we understand it, is wrapped up in coal, and your very excellent journal might do much towards educating public opinion to that end.

For this reason, I believe the proper place to make coal gas is at the coal pit—that gas should be supplied in a conduit pressure grid system to our towns. The burning of coal in the domestic grate is chemical vandalism; it polutes the air and destroys one of the most valuable assets of the future; in fact, industrial gas should displace coal for as many purposes as possible. Only in that way will abundant raw materials be available at a price to sustain it and only in that way may we become the largest exporters of plastic raw materials.

I believe in the democracy of the coal beds and in those black seams is the framework of an economic development that would provide for your wants.

There is one snag, however—four-fifths of the total carrying capacity of the railways consists in carrying coal (Sankey Report). The railway companies would be expected to put up a stiff opposition against the loss of their traffic—this is a useful example of vested interests as opposed to national interests.

I would have ended my comments on this note, but your remarks in respect to my criticisms on hydrogenation of coal call now for a more explicit explanation. At Midlothian in Scotland there are millions of tons of shale deposits. The great chemist Young was attracted to these deposits and from this shale he produced

petroleum, which was afterwards to become a very substantial business, producing thousands of tons per annum of fuel oil, petrol, burning oil, lubricating oil, paraffin wax, and, finally, sulphate of ammonia.

The shale, of course, has to be mined, and a thriving industry was built up—our wise legislators of the day taxed imported petrol, in order to encourage the home-produced article in Scotland. The financial manipulators, however, seized this delightful opportunity to negotiate the purchase of the controlling interests in the Scottish petroleum companies and to forthwith close the pits and throw thousands of miners out of employment.

They then transported their crude oil from abroad in tankers, discharged their cargoes at Grangemouth, and switched the refineries over to producing petrol from imported crude oil, and in that way avoided the tax. The shale oil was left to rot in the earth, the miners were paid off, whilst stockbrokers very gleefully distributed bonuses to their staffs.

There are millions of tons of oil contained in the deposits of the Scottish shales that can be profitably distilled or hydrogenated into petrol. The plant is there and the mines exist. Seamen and tankers, therefore, would be freed to continue their onerous duties elsewhere.

For that reason, and with all due deference to your very wise and enlightened self, I fail to appreciate the continuance of a subsidy being devoted to what, in my opinion, is a wasteful process applied to coal, which not only destroys the most valuable constituents in coal but also consumes a large proportion of a basic material which, according to the Minister of Mines, is likely to influence the winter comfort of each and all.—Yours faithfully,

HORATIO W. HUTTON.

Leicester.

[EDITOR'S NOTE.—We do not seem to be thinking on parallel lines, even now. We merely advocated pre-war carbide manufacture as a war-time insurance for acetylene, synthetic rubber and any polymer one chooses regardless of economic considerations. We believe that the system would have been justified. Mr. Hutton says (regarding our losses in Malayan rubber): "Not in our wildest dreams was misfortune such as this contemplated." Certain individuals, however, did foresee it. That is the whole point.

How heartily we agree with his ideas about coal and its real development. Nylon and polythene are absolutely up Great Britain's street. But why exclude "acetylene" plastics? As for the Pumpherston shale refineries, which we knew quite well, we were under the impression that they never paid even prior to 1914 and were only kept going because of the ammonium sulphate. However, we too are sorry they closed down, for they provided some of the finest technicians, who ultimately showed part of the world in Mexico, Persia and even the U.S.A. how to produce petroleum products.]

HANDBOOK OF PLASTICS

I notice on page 71 of your March issue an item concerning the need of a comprehensive reference book on plastics, and, accordingly, it may interest you to know that, in the early fall, D. Van Nostrand Co. will publish a plastics handbook by Mr. Carleton Ellis and myself which I believe will fill this need.

To give you some idea of its scope, I am enclosing a copy of the table of contents. HERBERT R. SIMONDS.

New York.

Part I.—Survey of the Industry.

Part II.—Physical Properties of Plastics. Test Methods for Physical Properties—Tables of Properties of Plastics.

Part III.—Materials. Ingredients of the Plastics Mix—Plastics Materials—Synthetic Textile Fibres—Elastomers—Films—Plywood.

Part IV.—Manufacture of Plastics. Manufacturing Processes—Resin Plant.

Part V.—Processing and Fabrication.

Part VI.—Chemistry of Plastics.

Part VII.—Applications of Plastics. Design of Plastics Parts.

Part VIII.—Commercial Considerations. Selection of Materials—Estimating.

Part IX.—Glossaries.

PRODUCTION NEWS

Raw Materials, New Plant, Works Organization, Control Apparatus, Research, Personal and Trade Notes

NAFTOLEN.—The Wilmington Chemical Corporation, of U.S.A., has put on the plastic market a group of hydrocarbon compounds under the trade name of Naftolen. They are purely hydrocarbon in nature obtained from petroleum residues, but are neither benzene-like or paraffin-like in constitution. They are also unsaturated, which means that they are reactive, quite neutral, good dielectrics and resinous or oily in appearance according to their molecular weight. "Modern Plastics" (April, 1942) describes their uses.

While they form no useful resins by reaction with formaldehyde, heating with both phenol and formaldehyde results in very useful plastic materials; this relates more especially to the production of laminated veneers. It is claimed that the effect of Naftolen is to increase mechanical strength, and where phenols and formaldehyde are scarce to make a saving in these chemicals. As an example is included the following table:—

	Naftolen-free Varnish. lb.	Naftolen Varnish. lb.
Cresylic acid	1,000	1,000
Naftolen	Nil	250
Formaldehyde (40%) ...	900	750
Ammonia (28%)	60	70
Resin yield	1,100	1,350
Alcohol	900	1,000
Varnish yield	2,000	2,350

SAFETY PRECAUTIONS.—In a paper entitled "Safety Precautions in Rubber and Plastics Machinery," presented before the American Society of Mechanical Engineers, Mr. J. Milward described the more recent developments in mechanical and other equipment that has been devised to eliminate accidents in the plastic milling of materials. The first mills had no power cut-out, no brakes and no method of stopping except by throwing an obstruction into the bite of the mills. The first important advance was the introduction of a throw-out clutch on the high-speed driving shaft. To-day both mechanical and electrical brakes are available. Another phase of the safety problem involves the proper arrangement of tripping mechanisms, e.g., safety bars and safety cables. It has also been proposed that mills be equipped with photo-electric cells so that an interrupted beam of light could actuate a brake.

PLASTIC CROCKERY.—Owing to the shortage of supply of domestic crockery the Board of Trade has made an Order controlling manufacture and supply. Captain Charles Waterhouse, Parliamentary Secretary to the Board of Trade, said recently: "We have cut exports by 20 per cent. and there will be a total cut of 40 per cent. by August. As a result we hope to put 80,000,000 pieces of utility crockery on the home market. We have called in the plastic trade to produce less breakable articles and that should yield another 10,000,000."

CRYSTALATE, LTD.—In order to avoid the partial loss of production and general dislocation over a long period which would be caused by the staggering of individual holidays, the works of Crystalate, Ltd., will be closed for one week from noon on Saturday, August 1, until 7 a.m. on Monday, August 10.

A nucleus office staff will be on duty from Tuesday, August 4, to Saturday, August 8, inclusive, to deal with inquiries, correspondence and urgent telephone calls.

COURTAULDS, LTD.—This company has returned to London from Maidenhead and is at the old address at 16, St. Martin's le Grand, London, E.C.1.

ERINOID, LTD.—This company has now obtained permanent London offices; their London offices and showroom will be situated at East India House, 208, Regent Street, London, W.1. The entrance to the new offices is in Foubert's Place, which is the south corner of Liberty's Building. Nearest tube station, Oxford Circus. Telephone: Regent 0418. Telegrams: "Erinoid Westdo, London."

W. R. ANSELL. His many friends in the plastics industry will wish Mr. Ansell the best of luck on leaving the offices of Temple Press Ltd., to join the R.A.F. At the beginning of the war he joined the advertising staff of "Plastics" and soon made a wide circle of friends amongst our advertising clientele. His interest in our industry went far deeper than mere "space-selling." Having a considerable knowledge of engineering he was invaluable to the Editor in making not only valuable contacts, but important suggestions.

Resinoids and Other Plastics as Film Formers

By B. J. BRAJNIKOFF,
Consulting Electrical Engineer

IX.—Styrene Polymerization Technique

AS has recently been shown by various workers, the physical behaviour of high molecular compounds, such as resins, rubbers, and the like, is primarily determined by the magnitude and geometrical configuration of macromolecules and only secondarily by the chemical nature of their constituents.

To the theoretical and experimental work of Ostromislensky we owe our early ideas on the mechanism of compound reactions; in his well-known researches on the polymerization of hydrocarbons, published in Russia in 1910-1916, Ostromislensky[91] was the first to advance the concept of multi-phase elementary processes in polyreactions, which he illustrated by a "step-wise synthesis of rubber-like products.

The novelty of such views in dissecting the complex reactions into partial processes will become even more apparent if we recall that the range of the chemical and physical methods available to research at the start of the present century was very restricted and scanty.

The main significance of Ostromislensky's investigations of high polymeric reactions attaches to the correct visualization of the problem, which, by arousing the interest of other scientists, led to far-reaching results.

As is known, subsequent developments in science confirmed Ostromislensky's opinion, and from that time, which may be considered as the foundation of Modern Chemistry of High Polymeric Systems, begins an arduous work extending the above ideas over a wide field of compound reactions, helped, in addition to delicate chemical methods, by the laborious devices of ultra-centrifuge, infra-red spectroscopy, X-ray, and, lately, electron diffraction techniques.

Nineteen hundred and twenty heralded the entry of another distinguished worker, Professor Staudinger[92] and his students, who greatly contributed to the unravelling of many knotty problems of high polymeric chemistry.

Styrene Polymerization in Retrospective

Before proceeding to the discussion of the current methods of styrol polymerization, a brief presentation of a few outstanding developments in the history of styrene polymerization may be justified.

The hundred years' span that has elapsed since Simon's observation in 1839 on the formation of styrene polymers has been marked by the following stages.

The first mention of the photochemical effect on styrol was made by Blyth and Hofman,[93] who found that light favours the polymerization reaction and that under the influence of heat metastyrol is depolymerizable to monostyrol.

The studies of Berthelot[94] in 1866 resulted in the discovery that polymerization of styrene can be carried out in solution form and that the process is affected by catalytic agents.

In 1878 Krakau[95] noticed that various substances (e.g., bromine, iodine, sulphur, etc.) can act as inhibitors of the styrene polymerization, with different degrees of effect.

A further contribution to the understanding of the styrene polymerization and its products was made at the close of the last century by Lemoine,[96] to whom belongs the first attempt to treat the reaction quantitatively. Lemoine established the fact of solubility of polystyrene in styrene and the possibility of their separation by fractional distillation in vacuo; 97 degrees C. was given by him

as the temperature level at which polymerization proceeds to completion. From the study of his experiments, Lemoine observed that the process can be activated by light, and particularly by the ultra-violet rays, but stops in the dark.

Contrary to these results, Stobbe and Posnjak,[97] who examined the polymerization of styrol, induced by radiation from a quartz mercury lamp, found that styrene, on being activated by light, displays a photo-chemical after-effect; i.e., it continues to polymerize in the dark. These workers were also the first to classify polystyrene as a colloidal body.

Colloidal Aspects of Polystyrenes

Extensive information on the formation of styrene polymers and the factors governing the rate of growth, size and shape of the resulting macromolecules may be obtained in the researches of Staudinger and his school.[98] Staudinger[99] found that the nature of the products of the polymerization of styrol is intimately bound up with the conditions under which they were formed. Thus, by conducting the polymerization process in the cold, in the absence of catalysts, it is possible to obtain very high molecular weight styrene polymers containing up to 1,000 monomeric residues in a polymeric molecule, whereas with the aid of such strong catalysts as stannic chloride, the degree of the polymerization of compounds formed usually does not exceed 100.

However, in the first case, the progress of the reaction is extremely slow (months and even years), resulting in the polymers of eucolloidal type which take a long time to swell and disperse in benzene, and yielding solutions and gels exhibiting high viscosity even in dilute state.

On the other hand, the low molecular styrene polymers of hemicolloidal type, with molecular weight less than 10,000, obtained at room temperature in presence of stannic chloride, display ready flow on heating, are easily soluble in benzene without swelling, forming solutions of low viscosity, but are very brittle. According to recent data,[100] this brittleness vanishes at molecular weights between 30,000-70,000, that is, from such molecular weights, which are characteristic of polystyrene products available on the market, as, for example, Distrene, Victron, Trolitul, etc. These polymers give relatively low-viscosity solutions, a feature of importance for the film-forming media, and are readily mouldable at moderate temperatures, yielding the final products of adequately high mechanical strength. As regards the conditions of the formation of these polymers, they vary, depending upon the method selected for effecting the polymerization.

Thus, it is known[101] that the viscosity and the average degree of the polymerization of styrene rapidly decreases as the temperature which induces its formation is raised, whereas the velocity of the reaction is thereby greatly increased.

Hence, by changing the temperature of the polymerization, polymers with the desired properties may be produced. It is to be noted, however, that both the polymerization speed and polymeric features derivable at a given temperature (e.g., viscosity and molecular weight), depend upon admixtures present in monomers, being conditioned by the quantity and nature of extraneous matter. For example, a negligible amount of antioxidant substances (phenols, amines, nitro-compounds) can strongly impede the polymerization process, whereas the presence even in minute proportion of oxygen of air and organic peroxides, quicken the polymerization and reduce the molecular weight of the finished product.

According to Schulz,[102] in the event of applying benzoyl peroxide as catalytic agent, the velocity of the reaction increases in direct proportion to the square root of the concentration of the catalytic substance; on the other hand, the degree of the polymerization changes in inverse ratio to the square root of the catalytic concentration, $\sqrt{C_{cat.}}$; consequently, the value $P.\sqrt{C_{cat.}}$ (where P signifies the mean degree of the polymerization) is constant.

On the other hand, it has been found

that, on dilution of styrene by toluol and other diluents, a reduction of the average degree of the polymerization, with the simultaneous retarding of the reaction, takes place; in cases, when polymers are not soluble in a diluent, it is observed that polymers are precipitated as soon as they are formed.

Hence, there are three ways by which the reduction of mean molecular weight of polymers and the viscosity of their solutions may be accomplished: (i) by means of increasing the temperature of the polymerization, (ii) by the addition to monomeric styrene of a catalytic agent, and (iii) by diluting monostyrene with a solvent; in the first two cases the reaction rate is increased, and in the last it is diminished.

Moreover, as demonstrated by Staudinger and Husemann,[102] by polymerizing styrol in its aqueous emulsions, the process is made to progress much faster than polymerization of pure styrol at same temperature, whereby, in spite of considerable increase of the reaction velocity, the molecular weight of polymers produced is not diminished. Thus, whereas pure styrene could be polymerized only after 1-2 months at 30 degrees to 60 degrees C., styrene emulsion, prepared by agitating styrene with 1 to 5 parts of aqueous solution of sodium oleate, at the same temperature range, was convertible in two to eight days into a stable latex-like suspension. From the latter polystyrene can be liberated in powdered form by acidifying or by the addition of alcohol.

As may be seen from tabulated data given in Section VII, molecular weights of styrene emulsion polymers exceed molecular weights of polymerization products of pure styrene obtained at identical temperature levels.

Hence the following polymerization methods may be used for the production of polystyrene on the industrial scale:—

(1) The polymerization of styrene in absence of diluents.

(2) Styrene polymerization in solution.

(3) Polymerization of styrene in aqueous emulsions.

In all three cases the reaction can be carried out either in presence of catalysts, or in their absence.

(1) Polymerization of Styrene in Absence of Diluents.

This polymerization method is characterized by the following features. On application of heat to styrene, free or catalyzed, it undergoes a gradual change from a mobile liquid to a hard vitreous mass (slab or block) taking the shape of the reaction chamber; the solid thus formed is transparent and absolutely colourless, if during the polymerization styrene has no access to the air.

If the product is not of very high molecular weight, it displays sufficient flow at 150 degrees to 200 degrees C., and after preliminary comminution, may be used for the preparation of coating and impregnating media in solution form, or mass production of crystal-clear and coloured articles of a required shape by injection moulding.

Since, however, the polymers themselves are not of the hemicolloidal type and are rather hard, their size reduction presents some difficulties and requires a special equipment.

Moreover, there is another reason for the comminution of polystyrene slabs; the presence of monomeric styrene which is usually found in a fairly large proportion in polymers, causes the ageing of final products, and, therefore, should be removed.

This can be effected by the prolonged heating of comminuted styrene in a drier at relatively low temperatures, since otherwise owing to thermal sensitivity of polystyrene, its baking into coherent body may occur; alternatively, the result may be obtained by heating the softened polymer at high temperature, for example, 200 degrees C., in vacuo.

Owing to tendency of the mass to turn solid before reaction is completed and the low thermal conductivity of polystyrene, regulation of the polymerization process in absence of diluents becomes difficult; as a consequence of local overheating of polymerizates, the formation of non-homogeneous products may result.

For these reasons the polymerization of styrene by this method can be effected best in flat-bottom vessels, which permit the production of polymers in the form of fairly thin slabs.

As to the temperature range of the polymerization, the process may be conducted at a constant temperature favouring the formation of polymers of the required viscosity, or the temperature may be varied as polymers are being produced, for instance, by raising it gradually, or, on the contrary, by heating monostyrene almost up to boiling point (146 degrees C.), till it begins to thicken, and terminating the reaction at a reduced temperature.

As is shown by experience, by adopting the procedure as just stated, it is possible to obtain colourless polystyrene of uniform quality with a relatively short polymerization time.

(2) Styrene Polymerization in Solution

A number of drawbacks incident to the preceding method may be obviated, if the polymerization of styrene is conducted in solution form. In this case, in the presence of an adequate amount of suitable solvent, for example, benzene or its homologues, the mixture remains liquid till the end of the reaction, with the result that the thermal control of the media presents no difficulties. However, with introduction of considerable quantities of solvent, the duration of the process increases, whilst the viscosity of the derived polymers decreases. Thus, for example, styrene, catalyzed by 0.25 per cent. of benzoyl peroxide, as a 1 per cent. benzene solution polymerized at 100 degrees C., within 14 to 16 hours, and gave polymers with the relative viscosity of 2.0-2.5; in presence of equal amount of ethylbenzene, the polymerization of styrene at 100 degrees C. took 40 to 60 hours to complete, and resulted in a brittle polymerizate of low viscosity (1.2-1.4), unsuitable either for coating field, or for mouldings.

This shows that monomeric styrene, in the state as it is made by the dehydrogenation of ethylbenzene (i.e., in the form of the solution containing about 50 per cent. of ethylbenzene), may not be employed to the best advantage for the production of polystyrene of appropriate quality, and should be separated from the solvent by rectification. Apart from this, the polymerization of styrene in solutions is complicated by the necessity of removing a solvent used from the derived polymers, for even the traces of the latter markedly decrease the heat stability of polymers, cause ageing, manifesting in such defects as fading of transparent articles and increasing brittleness during their storage.

In order to ensure a more uniform course of the reaction, which, being exothermic, is accompanied with a considerable liberation of heat, it is sometimes desirable to conduct the polymerization by the so-called continuous method.

The essence of the continuous procedure consists of a polymerization process that is not carried out to completion, but only partially, so as to render the suspension of polymers formed in solvent medium capable of flowing freely from the polymerizer through connecting pipes into a precipitating apparatus filled for that purpose with an alcohol.

The polymeric product conveyed into this auxiliary plant coagulates there as a powder, and unpolymerized monostyrene is returned back into the reaction vessel to be used again in the continuous polymerization process.

The polymerization of styrene can be carried out in such solvents which do not dissolve polystyrene, e.g., lower alcohols, and, therefore, promote its liberation during the polymerization.

However, in absence of a very large excess of diluent, the polymers are precipitated in the form of a viscous mass containing the monomeric styrene and the solvent, the removal of which is rather complicated. Consequently, this method of producing polystyrene offers no special advantages in comparison with the previously described procedure, the more so that in this case the reaction product displays low viscosity.

(3) Styrene Polymerization in Emulsions

Considerably greater interest attaches to polymerizing styrene in water emulsions prepared by homogenizing styrene with aqueous solutions of a number of emulsifying agents. This method has lately been the subject of detailed study at the Russian Institute of Plastics, where its successful operation was tested on a semi-industrial scale.

The emulsion method for producing polystyrene, compared with previously enumerated processes, possesses a number of advantages which, in the main, may be summarized as follows:—(i) The polymerization of styrene in water emulsions is much more rapid than in other media and lends itself to easy control and regulation. (ii) The monomeric styrene remaining in small quantities in the polymeric product, on termination of the polymerization, as well as other volatile admixtures, can be easily removed from the emulsion by steam distillation. (iii) The polymers may be produced either as latex-like systems, fitted for the direct application in coating field, or in the form of fine powder suitable for a further treatment depending upon the object in view. The physical and processing qualities of polymers so obtained are especially useful for the manufacture of film-forming and impregnating compositions by dissolving them in proper solvents, or in any other desired manner, as thermo-spraying etc. Polystyrenes are soluble in coal-tar hydrocarbons, organic compounds containing chlorine—and nitro—groups, and cyclohexanones; they are completely unaffected by alcoholic solvents, acetone, glycol ethers, petroleum hydrocarbons, and most acids and alkalies.

These polymers can give tough films either perfectly colourless, water-clear and fadeless, or may be modified by mixing with various fillers, pigments, and other substituents as required. They are, of course, excellent materials for injection moulding and other fabrication technique.

The polymerization of styrene by the emulsion method is conducted in an enamelled apparatus fitted with a stirrer, reflux condenser and steam jacket.

After preparing the solution of emulsifying agent, the monomeric styrene with a suitable catalyst (e.g., peroxides of hydrogen or benzoyl) are then introduced, while vigorously agitating the mixture. Soap (about 4 per cent. of the weight of styrene) may be used as an emulsifying agent, as well as polyvinyl alcohol, gelatine, and other substances. By polymerizing a system, where soap is used, a very stable emulsion is obtained, which may be destroyed by acidifying of the mixture, addition of alcohol, or by freezing, whereas in the case of applying gelatine or polyvinyl alcohol, the polymers are released and settle down in the shape of tiny grains already during the polymerization process. The duration of the polymerizing reaction effected at 80 degrees to 90 degrees C. in presence of catalyzers, is usually of the order of four to seven hours, after which the traces of monomeric styrene are distilled off with steam and (in the event of using soap emulgent) the colloidal solution is subjected to coagulation. The precipitated layer of polystyrene is then washed with water, to remove acids and salts, and with alcohol to free it from fatty acids, and afterwards dried in vacuo at 50 degrees to 60 degrees C. for 10-12 hours.

When gelatine or polyvinyl alcohol are used as emulgators, they are washed from polymers with water. However, in these cases, a slight discoloration sometimes observed in articles made from them testifies to the difficulty of liberating polystyrene from emulsifying agents and stresses the necessity for their complete removal. Their presence also leads to other after-effects.

Thermo-polymerization of Styrene and its Inhibition

A very important aspect of the styrene polymerization technique is stabilization and inhibition procedure, by adding various substances which are capable of exerting an influence, in a greater or lesser degree, upon the induc-

tion period of molecules and thereby change the overall reaction rate.

The latest studies[104] indicate that in this respect different bodies may be divided into the following groups:—(i) catalysts, (ii) completely non-reactive or neutral substances, (iii) reagents that delay the polymerization by extending the induction period or induce the reaction to proceed at slow rate, (iv) components, the presence of which gives rise to a certain well-defined induction period (e.g., for 240 or not less than 600 hours at 60 degrees C.), after which the reaction rate attains maximum and resumes its normal course.

The stabilizers of the polymerization denote substances which ensure a more or less long induction period.

The stabilization of styrene can be effectively performed by members of the groups: quinonoids, phenols, amines and nitro-compounds.

The duration of the induction period is directly proportional to the concentration of the added substance:—

Quinone. Per cent.	Induction Period. Minutes
0.02	30
0.05	70
0.10	130
0.20	270

When it is desired to avert or retard the polymerization, as during distilling operation for purifying the product, or in storage and transportation, the selection of a stabilizer is guided by: (a) the length of the induction period required for de-activating styrene molecules, after which they are allowed to regain their normal activity, and (b) the possibility of removing stabilizer without undue difficulty.

It is clear, therefore, that the results of the above work are instructive not only for the polymerization technique as such, but they open up further avenues for investigating resinification kinetics. The reaction that forms the basis of the induction period (the length of which is the linear function of the concentration of the stabilizer) is monomolecular: the molecule of styrene is de-activated by collision with the molecule of inhibitor; the polymerization may restart only after all molecules of the stabilizer are used up. The idea that molecules of the inhibitor enter into the structure of polymeric chains should be rejected on the ground that the stabilizer usually can be with ease removed unaltered.

Chemistry of Polystyrene Formation

The actual nature of resinifying phenomena is extremely complex, and the fact that all theories so far propounded fail to agree with the results of experimental observations, testifies that, until knowledge of atomic and intramolecular structure is further advanced, it is unlikely that a satisfactory interpretation will be found.

One thing emerging clearly is that styrene resins are linear polymers of monostyrene units combined by the fundamental valence forces through the opening of their ethylenic double bonds.

According to Staudinger, these polystyrene chains, which are characterized by a large ratio between their molecular weight and cross-section, and are soluble and fusible, may, under certain conditions, aggregate into three-dimensional macromolecules, resulting in the radical decrease of their solubility and swelling. As a non-polar resin, polystyrene is soluble in non-polar solvents and absorbs practically no water.

A good deal of information may be found in Ostromislensky's work on the mechanics of resinification of styrene, which, since 1925, was performed by him in the U.S.A. The practical results of his discoveries on improved polymerization methods, reaction velocities and resultant products are embodied in a number of instructive patents.[105]

The modern concept of styrene polymerization phenomena, based upon the evidence of the latest research, as expounded by Mark, Raff and co-

workers,[106] may be summarized as follows:—

The total process by which styrene molecules, under the action of heat or light, lead to the production of polystyrene macromolecule, is expressible in a generalized form as: n × (CH_2 = CH—C_6H_5) —> (CH_2—CH—C_6H_5) n, where n (100 to several thousands) is a number of monostyrene units linked together into polystyrene chains of different lengths, which can be extensively branched, varying statistically with the conditions of the polymerization procedure.

Since it is inconceivable that such high molecular complexes are formed in a single stage, it is thought that these polyreactions involve several individual processes, consisting of:—

(1) Initiation reaction, the phase, rich in energy interchange, absorption of quanta, etc., due to primary activation of the ethylene double bond and giving rise to formation of chain nuclei.

(2) Propagation process, effecting the growth of chains, or the polymerization proper.

(3) Branching process owing to lateral addition.

(4) Termination reaction due to de-activation of molecules, and resulting in breaking up, disruption, or cessation of chains.

Staudinger and Frost[107] pointed out that polystyrenes formed at the start or at the end of the reaction display, practically, identical viscosity and thus equal mean degree of the polymerization; further work of Schulz and Husemann[108] showed that, although the time needed for starting the nucleus formation may vary from a few hours to many days, depending on thermal régime, the period required by the chain, once activated to reach its final size, is very brief.

The foregoing observations suggest that these concurrent elementary processes of chain growth and termination interact and condition each other, which is of importance in application to styrene polymerization problems on the industrial scale.

Properties and Applications of Polystyrene

As has been stated previously, the characteristics of polystyrenes depend upon conditions of the polymerization under which they are produced. The polymers of styrene which are suitable for industrial purposes were the subject of intensive studies by many workers and the data on their basic properties has now become available in considerable detail.

Thus, for example, according to Staudinger and Stanley,[109] the technical polystyrenes, which are included by them in the group of mesocolloids, are characterized by the following physical properties:—

Specific gravity	1.05-1.06
Hardness (mineralogical scale)	2-3
Refractive index	1.668
Water absorption (per cent.)	0.0 to 0.02
Coef. of linear expansion	0.0001
Resistance to bending	840-1,050 kg./cm.^{2}
Tensile strength	420-490 kg./cm.^{2}
DIELECTRIC PROPERTIES.	
Spec. vol. resistivity, ohms/cm.^{3}	> 10^{18}
Surface resistivity, ohms/cm. (after 24 hours in water)	> 10^{16}
Dielectric strength (3 mm.)	20 kv/mm.
Dielectric strength (0.25 mm.)	48 kv/mm.
Permittivity at 50 cycles	2.5
Permittivity at 800-750,000 cycles	2.4
Power factor (tan δ) at 800 cycles	0.0001
Power factor (tan δ) at 750,000 cycles	0.0002

In dielectric properties, polystyrene excels any other synthetic resins, for which reason it is finding an increasing application in electro - technology. Furthermore, this material possesses a number of other features (e.g., compatibility with other resins, etc.), which render its utilization in other branches of industry very valuable. The decorative effect due to pleasing appearance of products derived from polystyrene was instrumental in the expanding demand for highly artistic articles of every description, including household.

As a thermoplastic material, polystyrene is readily mouldable, and at the temperature range from 120 degrees to 140 degrees C. under 100-200 kg./cm.^{2} pressure, it is excellently suited for various operations, particularly for mass-produced

articles of small size, by the injection process, requiring in most cases no addition of plasticizing agents.

Pure polystyrene resin is distinguished by the possession of a very high modulus of elasticity and stability to variations of temperature and humidity. Polystyrene changes very little after heating during 120 days at 50 degrees C., or for 25 days at 70 degrees C.

Film-forming Developments

In addition to pure polystyrene, its mixtures with different fillers, for example, quartz, talc, marble, etc., may be used to advantage. The basic requirements of fillers, in cases of electrical applications, must, obviously, be that they should not appreciably lower the dielectric properties of polystyrene. It is claimed by some workers that styrene polymers cannot be plasticized by any substance having a zero electric moment. Should such claims be finally confirmed, it follows that it may not be possible to plasticize polystyrene by the direct incorporation of any substituent without degrading the dielectric characteristics of the resultant product.

A satisfactory way out of this uncertainty has recently been found by the development (in Germany) of the new polystyrene material designated Styroflex,[110] produced from polystyrene under the pressure of 50 to 100 atmospheres, by subjecting it to a purely mechanical treatment dispensing with plasticizers, and yielding the material distinguished by exceptional elasticity.

The films derived from Styroflex for the use on electrical condensers and fibres[111] for braiding flexible co-axial conductors and high-frequency cables, as well as other compositions show outstandingly high insulating power.

Although the overall mechanical strength properties of Styroflex fibres as yet do not reach parity with the natural silk or cotton fabrics, it is unlikely that the research worker will fail to fill the gap, as the trend of recent patents already testifies.[112]

The manufacture of the flexible polystyrene fibres has attracted the attention of electrical engineers, particularly in Great Britain, U.S.A. and Germany, where they find expanding demand in the cable industry, especially for marine service.

Polystyrene Filaments

The Styroflex filaments and films are produced by extruding polystyrene mass heated up to 180 degrees to 195 degrees C. through narrow orifice with simultaneous strong stretching.[111]

Polystyrene film-forming systems, impregnants, varnishes, and the like, are prepared either by dissolving styrene polymers in benzene, toluol, xylol, carbon tetrachloride, and other non-polar solvents, or by polymerizing styrene in these solvents, or in aqueous emulsions. On evaporation of solvent, these compositions give coatings, that are distinguished by the properties inherent to polystyrene resins.

The preparation of a filled polystyrene can be accomplished by: (a) the polymerization of styrene in the mixture with a filler; (b) mixing a filler with the polystyrene varnish; and (c) grinding the polystyrene with a filler in a ball or roller mill.

Polystyrene film-forming media can be produced either as transparent, glass-clear, or coloured to any desired shade, yielding exceedingly fine continuous coatings. Perfect homogeneity and transparency render them particularly useful in application to aeronautical instruments and other devices.

High dielectric properties of styrene resin, namely outstandingly low electrical power factor, great disruptive strength, arcing resistance and non-hygroscopicity, are not altered even at temperatures very near to the softening point of the material, which is of special importance for insulation in high-tension service and radio-engineering.

The utility of polystyrene as insulating material, in the form of very fine films, may be exemplified by the proved performance of Styron developed lately by the Dow Chemical Co.,[113] U.S.A., styrene

coatings of the International General Electric Co.,[114] of New York, and others.

Recently, by co-polymerizing styrene with butadiene a new synthetic rubber-like plastic has been evolved, which in many respects (e.g., resistance to abrasion, etc.), is superior to the natural rubber. By virtue of these important properties it is already taking a leading part among synthetics, being produced in large quantities in Germany (Buna S) and in the U.S.A. by such concerns as the Standard Oil Co., of New Jersey, and the Firestone Tyre and Rubber Co.[115]

(To be continued)

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BURNING TESTS OF PLASTICS

(Continued from page 209)

unburned portion. The cast phenolic and the cotton-filled moulded phenolic plastics were somewhat more difficult to ignite than the casein plastic, but once ignited propagated the flame over their entire length. The wood-filled moulded phenolic plastic burned for only a short time after ignition, and the flame was not propagated to the unburned portion. One sample of urea formaldehyde plastic, although difficult to ignite, propagated the flame over its entire length, whereas the other sample burned for a short time at the point of ignition and then went out. One specimen of plasticized vinyl-chloride, vinyl acetate copolymer ignited rather easily and burned with a feeble flame, which was easily extinguished by a slight draught. Thus, although combustible, the particular compositions appear to be much less burning than those of Group 1.

In Group 3 those plastics were placed which did not propagate the flame after the removal of the test flame. In this group are included cold-moulded plastic, plasticized poly-vinyl chloride, two samples of plasticized vinyl-chloride acetate copolymers, three samples of unplasticized vinyl-chloride vinyl acetate copolymers, the asbestos-filled moulded phenol resin and one sample of plasticized polyvinyl alcohol.

General Conclusions

The relative combustibility of a plastic composition depends not only on the synthetic resin used but also on the plasticizers, fillers and pigments incorporated in it. This is vividly demonstrated by the difference in the behaviour of the two polyvinyl alcohol samples, from which one was grouped in No. 1, the other in No. 3. The effect of the filler is well illustrated in the case of moulded phenol resin, cotton- and wood-filled ranging in No. 2 and asbestos-filled in No. 3.